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THE UNIVERSITY OF ALBERTA

A THERMODYNAMIC MODEL FOR AQUEOUS FOOD SOLUTIONS

by

©

Neal S. Lee

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF Master of Science

IN

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Department of Food Science

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Spring 1987

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Supervisor

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Date... March 31, 1987

ABSTRACT

A model for the excess Gibbs energy of a representative food solution is presented. The solution consists of water, ethanol, sucrose and sodium chloride. The model is based on an extended UNIQUAC equation presented by Christensen and his colleagues (1983) for the excess Gibbs energy of multicomponent solutions containing both electrolytes and non-electrolytes. The expression divides the excess Gibbs energy into contributions from three sources : long-range ionic forces describing the electrostatic interactions between ions, short-range forces between all species and a contribution describing structural effects in the solution. The long-range forces are described by the Debye-Hückel limiting law extended with a virial term. The short-range interactions and the structural effects are described by the UNIQUAC equation (Abrams and Prausnitz, 1975) a local composition based equation.

The required model parameters are taken from the literature or optimized based on experimental data. With the optimized parameters, the experimental component activity coefficients in the aqueous binary and ternary sub-systems are correlated accurately over a wide concentration range. The model is also used to correlate the solubility of three terpenes in aqueous sucrose solutions.

The predicted activity coefficients are used to calculate freezing point depression, boiling point elevation, solute solubilities and vapour-liquid equilibria in

selected binary and ternary sub-systems. Using the model, these properties are predicted accurately in solutions of low to moderate solute concentration.

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List of Symbols

A	Debye-Hückel parameter (eqn 3.3.4)
a	activity
a°	ion size parameter
B_{solv}	Brønsted-Guggenheim solvent parameter
b	Debye-Hückel solvent parameter (eqn 3.3.5)
c	physical constant (equation 3.3.4)
f	fugacity
G	Gibbs energy
H	enthalpy
$H^{o}_{s,l}$	partial molar enthalpy of solute
$H^{o}_{s,s}$	molar enthalpy of solid
$\bar{h}$	partial molar excess enthalpy
J	flux
K_{ij}	Mass transfer coefficient
l_k	bulkiness parameter
M	molecular weight
m	molality (mol kg solvent^{-1})
m'	aqueous molality (mol kg water^{-1})
m^{θ}	standard molality value (eqn. 11.3.1)
n	number of moles or number of points
P	pressure or partial pressure
q	pure component surface area parameter
R	universal gas constant
r	pure component volume parameter
S	entropy
$\bar{s}$	partial molar entropy

T	temperature (K)
t	temperature (C)
U_{ij}	UNIQUAC potential energy parameter
$\bar{v}$	partial molar volume
W	weight fraction
W'	water-free weight fraction
w	weighing parameter
x	mole fraction
x'	salt-free mole fraction
Z	charge number
z	coordination number

Greek Letters

β	Brønsted-Guggenheim specific-ion interaction parameter
γ	activity coefficient
ϵ	dielectric constant
ΔH_f	enthalpy of fusion
θ_f	freezing point depression
θ_b	boiling point elevation
θ_i	component surface area fraction
μ	chemical potential or partial molar Gibbs energy
ν	stoichiometric coefficient
π	osmotic pressure
τ	UNIQUAC interaction energy parameter
ρ	density
ϕ	osmotic coefficient
ϕ_i	component volume fraction
ϕL_s	relative partial molal heat content

ϕH_s	apparent molal enthalpy
χ^2	Chi-square statistic

Subscripts

a	anion
c	cation
EtOH	refering to ethanol
l,l'	liquid state
m	molal basis
o	standard state
s	solid state, solvent or sucrose
suc	refering to sucrose
v	vapour state
w	refering to water

Superscripts

BG	refering to the Brønsted-Guggenheim term
DH	refering to the Debye-Hückel term
UNI	refering to the UNIQUAC term
E	excess
*	refering to unsymmetric convention
∞	infinite dilution
0	zero concentration; all solutes

1. INTRODUCTION

The engineering design and development of food processes requires thermophysical and transport properties of the materials involved. With the "computer revolution" a new and powerful instrument has become widely available for this purpose. The use of numerical simulations has provided the engineer with a tool with which processes may be optimized with much more precision than was previously possible. With the application of numerical techniques however, comes the need for thermophysical properties under different conditions of temperature, pressure and composition. For food processes, the variations with temperature and composition are of greatest importance.

One cannot hope to measure more than a tiny fraction of the physical properties needed for engineering process design, hence one must predict, correlate and compute them (Larsen, 1981). It is in this area that the science of thermodynamics may be applied.

Thermodynamics and the thermodynamic representation of solutions provides a tool with which measured properties of a system may be used to calculate other properties through well-established thermodynamically consistent relationships, thereby allowing the prediction of a desired property under different conditions without the need for experimental measurement. An accurate thermodynamic model for food solutions will allow the prediction of its variation with different process variables. The thermodynamics of food systems is, however, a very complicated matter.

The materials involved in food processes are usually biological in origin; the major constituent of such systems usually being water. Thus, most food systems may be represented by complex, multicomponent aqueous solutions. These solutions contain a wide variety of components, including salts, minerals, carbohydrates, lipids, proteins, alcohols, and aromatic compounds. In addition, many of the components present in minute quantities are vital in the organoleptic characterization of the food, and their behavior must be well reflected by any thermodynamic model developed to characterize food systems.

The behaviour of these compounds must be considered when the effects of food processing operations on food quality are assessed. The distribution of flavour and aroma components, such as terpenes, ketones and esters, between the vapour and liquid phases and between immiscible liquid phases, and the variation of this distribution with temperature, pressure and composition must be known to determine the true composition of the food after such operations as freezing, freeze drying, evaporation, distillation and membrane separations (Le Maguer, 1981). There is a need for an accurate thermodynamic representation of food solutions to effect any improvements in the design and simulation of food processes.

Examples of processes commonly found in food operations that would benefit from a thermodynamic model include:

distillation, evaporation and drying, which depend on vapour-liquid-solid equilibria. In the liquid phase, modeling of the solvent extraction of commodities (such as oil seeds, coffee, cocoa beans and sugar beets), osmotic dehydration, pickling, and desalting processes, and membrane separations would all be improved with better representation of liquid phase equilibria. A better description of solid-liquid-vapour equilibria would greatly benefit the modeling of processes such as crystalization, freeze concentration and freeze drying.

An added dimension to the thermodynamic characterization of food materials is the importance of water activity as a major parameter affecting the quality and stability of foods. Water activity has been found to be a major factor influencing the microbial (Troller, 1979), chemical and biochemical stability of most foods (Labuza, 1980). It has been found to influence processes such as enzymatic activity and free radical formation and distribution (Drapron, 1985; Troller and Christian, 1978). Methods used in the food industry for the estimation of water activity in foods are relatively simple, based primarily on the application of Raoult's Law to food systems. In fact, the limited application of the thermodynamics of phase equilibria to food processing is primarily in the application of Raoult's Law and the subsequent estimation of physical properties such as freezing point depression and boiling point elevation of the food system based on the estimated water activity. Osmotic pressures often used as driving processes in membrane processes are also calculated from water activities. The importance of the water activity as a quality parameter for food systems has been illustrated, despite its importance however, only very simple methods for its calculation are used in the food industry.

Thermodynamic models for phase equilibria have been extensively applied in the field of chemical engineering, resulting in significant improvement in the design and simulation of many industrially important chemical processes. A review of the chemical engineering literature reveals that, although models exist for thermodynamic representation of many industrially important systems, these systems are of a fundamentally different nature than those encountered in food processing applications. Well established models exist for application to either non-electrolyte solutions or aqueous electrolyte solutions. Most of these models are semi-empirical in nature, containing adjustable parameters that must be estimated based on experimental data. In more complex systems, containing both electrolytes and non-electrolytes, phase equilibria is still approached largely at a qualitative and empirical level, with most equilibrium data obtained experimentally.

Recently, a number of models have been presented which attempt to bridge the gap between aqueous electrolyte and non-electrolyte solution modeling. There has been limited success in the thermodynamic representation of aqueous mixed electrolyte solutions (Christensen *et al.*, 1983; Cruz and Renon, 1978; Chen and Evans, 1986), and the application of these models to solutions of electrolytes in mixed solvents has just begun (Sander *et al.*, 1986a,b,c; Mock *et al.*, 1986) and is still developing.

The objective of this work is the modification of a thermodynamically based model for phase equilibria for application to simple food systems. A model presented by Christensen and his coworkers (Christensen *et al.*, 1983) based on the UNIQUAC equation (Abrams and Prausnitz, 1975; Maurer and Prausnitz, 1978) for applications to systems of electrolytes in mixed aqueous solvents is the basis of this work. A simple solution, representative of an aqueous food system containing sodium chloride, sucrose, ethanol and water is selected to test the suitability of the selected model to food solutions. After validation, applications of the model to the prediction of physical properties and the modeling of mass transfer processes are illustrated.

2. THERMODYNAMIC MODELING OF PHASE EQUILIBRIA: A REVIEW

The application of thermodynamic modeling techniques to food systems is a complex problem. In this review, applications of thermodynamic modeling to food engineering will be discussed, with particular attention to the prediction of water activities of food solutions. A general review of the thermodynamic modeling of fluid phase equilibria will be presented. This will be followed by the description of some of the models used in the chemical industry to represent the behavior of non-electrolyte solutions and their thermodynamic basis. Since the presence of ions in a solution drastically affects its thermodynamic behavior; the development of models describing the behavior of aqueous electrolyte solutions will be reviewed. The chapter will conclude with a discussion of the thermodynamic modeling of electrolytes in mixed solvents.

2.1 Thermodynamic Modeling of Food Systems

The application of thermodynamic models to food systems has been motivated primarily by Scott's observation (1957) that it was not the water content *per se* which was the important parameter in the assessment of the availability of water for different deteriorative reactions in foods, rather it was the water activity. With the development of intermediate moisture foods (IMF) and knowledge of the effect of water activity on the microbial and physio-chemical stability of IMF (Troller, 1979), new applications for these models were found.

2.1.1 Prediction of water activities

A number of semi-empirical equations have been proposed for the calculation of water activities (a_w) of food solutions (Norrish, 1966; Sloan and Labuza, 1976). Ross (1975) presented an equation for the prediction of water activities of aqueous solutions of soluble solutes based an a simplification of the Gibbs-Duhem equation. In this simplification, it was assumed that no interactions occured between solutes. Chuang and Toledo (1976) presented a modification of Norrish's equation (Norrish, 1966), in which water activities of binary solutions were fitted as linear functions of the solute mole fraction. A method through which the linear coefficients of the binary mixtures are combined to predict the water activities of multicomponent solutions containing insoluble solids was developed.

More recently, a number of models for aqueous solutions of strong electrolytes used in the chemical industry have been adapted for application to food systems. These models are used for intermediate moisture food systems to compare the a_w lowering effect of different solutes. Benmergui and coworkers (1979) used Pitzer's equation (Pitzer, 1973) to predict a_ws in a number of aqueous solutions of "food additive like" strong electrolytes. Ferro-Fontán *et al.* (1979) used the Bromley equation (Bromley, 1973) for the same purpose. This equation is a single parameter equation and has the advantage of allowing direct comparisons of potential a_w lowering agents.

A number of modifications to the Ross equation have been presented (Ferro Fontán *et al.*, 1981; Chirife *et al.*, 1980) which allow the prediction of the water activities of mixed electrolyte-non-electrolyte solutions. These equations have been applied to the prediction of a_w in some food systems; including juices (Ferro-Fontan *et al.*, 1981) and sugar solutions representative of honey (Rüegg and Blanc, 1981). Favetto and coworkers (1981a,b), in their study of the dehydration of beef slices by immersion-cooking in aqueous sodium chloride-glycerol solutions, used the Ross equation to estimate the variation of the a_w of the beef slices with different process variables.

Most of the work in the application of thermodynamic models to food systems has been centered on the prediction of their water activities. This is clearly due to the importance of this quantity as a parameter of food stability. For the application of process modeling techniques to food processes, a thermodynamic representation of each component in the system is required. The thermodynamic representation of a single component is not sufficient for this purpose.

2.1.2 Thermodynamic modeling of aroma compounds in food systems

In the thermodynamic modeling of food systems for the assessment of the effects of different processes on the food materials, the majority of the work done has been in the modeling of the behavior of aromatic compounds in model food systems. Such compounds are important in the determination of the organoleptic quality of foods. Le Maguer (1981) used the UNIQUAC equation (Abrams and Prausnitz, 1975; Maurer and Prausnitz, 1978) to model the behavior of the terpene-water system, with good results. It was stated that it is important to know the nature and composition of the phases that appear when one cools, heats or removes water from actual foods to determine the true composition of the food after such operations as freezing, freeze drying, evaporation, distillation and membrane separations.

Lebert and Richon (1984) cite the work of Allaneau, who used a number of non-electrolyte thermodynamic models to predict the infinite dilution activity coefficients of some aromatic compounds in solutions of olive oil from experimental data.

Sorrentino and coworkers (1986) used the ASOG (Derr and Deal, 1968) and the UNIFAC (Fredenslund *et al.*, 1975) equations to predict the activity coefficients of aroma compounds in water-carbohydrate and water-polyethylene glycol solutions at various concentrations. Using literature values for the group interaction parameters in the two models, neither equation was able to predict the experimental activity coefficients with sufficient accuracy. New values for the group interaction parameters were proposed to facilitate the application of the ASOG model to these systems.

2.1.3 The need for a complete thermodynamic treatment

A complete thermodynamic treatment of food systems would allow the prediction of the physical properties, such as boiling points, freezing points and solubilities. Presently, even in the most technologically advanced industries, such as the sugar industry, these properties are obtained from tables of experimental data (Honig, 1953; Hugot, 1972). A numerical method for the calculation of these properties is also easily amenable to use in computer calculations, allowing the full utilization of these techniques in food process design.

The modeling of multicomponent mass transfer in biological systems has been the subject of recent research (Toupin, 1986; Guenneugues, 1986). In these works, mass transfer was approached from the standpoint of irreversible thermodynamics based on the work of Katchalsky (1963). With such an approach, a thermodynamic description of the multicomponent systems is required for a description of the driving forces involved. A thermodynamic treatment for food systems has not yet been developed. Thermodynamic models exist and are commonly used in the chemical industry. The basis of these models will be reviewed to evaluate the feasibility of their adaptation to food systems.

2.2 Thermodynamic Modeling of Fluid Phase Equilibria

Chemical and food processes commonly occur under conditions of constant temperature and pressure; because of this, thermodynamic models for phase equilibria are most often based on expressions for the excess Gibbs free energy of the mixture as a function of composition (Prausnitz, 1977), the excess Gibbs energy being the pertinent thermodynamic quantity under these conditions. These expressions must meet a number of boundary conditions at the limits of concentration which are dictated by the thermodynamic definition of the excess Gibbs energy.

2.2.1 Simple expressions for the excess Gibbs energy

The simplest, non-trivial expression for the excess Gibbs energy of mixtures is the Two Suffix Margules equation. This equation expresses the Gibbs energy as the product of the mole fraction of each component and an empirical constant which is a function of the system temperature (Prausnitz *et al.*, 1986). A few simple systems are represented well with the Two Suffix Margules equation.

A number of authors have extended this equation in a series expansion to reflect the complexity of real solutions. Among these expressions, the Wohl expansion (1946) and the Redlich-Kister expansion (1948a,b) are most notable. The advantage of the Wohl expression is its easy extension to multicomponent solutions and the physical significance attached to the parameters which appear in the expansion (Prausnitz *et al.*, 1986). The Van Laar equation is a truncated Wohl equation for the excess Gibbs energy. This equation has been very popular due to its flexibility and mathematical simplicity (Van Ness and Abbot, 1982). The Redlich-Kister expansion, aside from being a method for representing liquid phase activity coefficients, may also be used to classify different types of liquid solutions (Prausnitz *et al.*, 1986). Most of the simple models for the excess Gibbs free energy of mixtures are empirical in nature, requiring parameters estimated from experimental data.

2.2.2 Local composition models

The introduction of the concept of local composition to the thermodynamic modeling of phase equilibria resulted in the development of a whole new family of models. The concept of local composition is based on the non-randomness concept of the quasi-chemical theory of liquid mixtures developed by Guggenheim (1952). It was, however, the introduction of Wilson's (1964) definition of local composition that resulted in its wide use in expressions for the excess Gibbs energy of liquid mixtures. In Wilson's model, non-randomness in liquid mixtures was taken into account by considering the local composition around each individual molecule. Wilson's expression is based on the Flory-Huggins expression for athermal mixtures, replacing the overall segment fraction with the local volume fraction. The introduction of the local composition concept has prompted the development of many flexible and powerful models for excess Gibbs energy models used today (Rasmussen, 1983), a few of which will be briefly reviewed.

Renon and Prausnitz (1968) used a modified form of Wilson's local composition concept to derive the NRTL equation. The NRTL (non-random, two liquid) equation gives an excellent representation of many types of liquid mixtures and has the ability to predict ternary vapour-liquid and liquid-liquid equilibria based only on binary data. It is also very easily extended to ternary or higher multi-component mixtures.

Vera *et al.* (1977) proposed two new expressions for the excess Gibbs free energy of liquid mixtures derived from Guggenheim's quasi-lattice model and Wilson's local composition model. These equations, termed the Local Surface Guggenheim (LSG) and the Local Composition Guggenheim (LCG) equations require two adjustable parameters per binary. No higher order parameters are required for their extension to multicomponent systems. A systematic method for the evaluation of pure component structural parameters required by the LSG and LCG equations was presented along with results from the application of these equations to a number of non-electrolyte systems.

2.2.3 The UNIQUAC equation

Abrams and Prausnitz (1975) presented a local composition model based on the generalization of Guggenheim's quasi-chemical treatment, through the introduction of the local area fraction as the primary concentration variable. Their equation, called the UNIQUAC (universal quasi-chemical) equation is applicable to mixtures of polar and non-polar components and to mixtures in which the molecules differ appreciably in size and shape. It can be used to represent both vapour-liquid and liquid-liquid equilibria of multicomponent solutions based only on binary parameters.

In the UNIQUAC equation, the excess Gibbs function is given as the sum of two terms: a combinatorial term and a residual term. The combinatorial term represents the entropic contribution to the excess Gibbs energy of the solution. It is determined from the composition, a parameter z, representing the coordination number of the lattice, and parameters representing the volume (r_k) and surface area (q_k) of the component molecules. These parameters may be estimated from pure component data on molecular crystals (Abrams and Prausnitz, 1975). The residual contribution takes into account the non-idealities in the solution due to intermolecular interactions; these interactions are responsible for the enthalpy of mixing (Prausnitz *et al.*, 1986). The residual part of the equation requires two adjustable parameters per binary, characterizing the potential energy of interaction between the solution components. The combinatorial contribution represents the athermal entropic contribution to the excess Gibbs energy, and as a consequence all temperature variation is accounted for in the residual term (Prausnitz *et al.*, 1986).

Inconsistencies in the derivation of many local composition models based on a one-fluid lattice model, pointed out by McDermott and Ashton *et al.* (1977) and Panayiotou and Vera (1981) have been eliminated from the derivation of the UNIQUAC equation in a separate derivation based on a two-liquid model (Maurer and Prausnitz, 1978). The UNIQUAC equation gives good representation of the excess Gibbs free energy of a large variety of binary liquid mixtures (Rasmussen, 1983). It is readily generalized to multicomponent mixtures although with somewhat less success, partially due to the semi-empirical nature of the equation. Molecular-dynamic calculations suggest that the non-randomness assumption is too strong (Fischer and Kohler, 1983; Hu *et al.*, 1983). Although the basic principles of the equation are useful, significant modifications are required to provide the UNIQUAC model with a sound molecular basis (Prausnitz *et al.*, 1986). The flexibility and reliability of the UNIQUAC equation in the representation of both the vapour-liquid and liquid-liquid equilibria of a large number of binary systems, along with its straightforward extension to multicomponent systems, has prompted a number of researchers to attempt to modify the equation for application to a larger number of systems. Most of these modifications are empirical in nature and specific to certain types of systems. They do, however, reveal some of the deficiencies in the model and it is perhaps illustrative to review some of these modifications at this time.

2.2.4 Modifications to the UNIQUAC equation

Anderson and Prausnitz (1978a,b), in their evaluation of pure component UNIQUAC parameters for 90 pure fluids and a number of binary systems, presented an empirical correction to the surface area parameter in the residual contribution to the excess Gibbs energy to be applied to systems containing alcohols or other polar species.

Skjold-Jørgenson *et al.* (1980), in attempting to use the UNIQUAC equation for the simultaneous representation of both the excess Gibbs energy and excess enthalpy of liquid mixtures, presented a modified UNIQUAC equation with a temperature dependent coordination number. The modified equation is shown to represent both the excess Gibbs energy and the excess enthalpy of a number of systems using a unique set of parameters. By allowing the interaction energies to vary with composition, Skjold-Jørgenson *et al.* (1982) modified the UNIQUAC equation to consider association and solvation effects in the simultaneous representation of vapour-liquid and liquid-liquid equilibria.

Kikic *et al.* (1980) and Alessi *et al.* (1982) modified the athermal, combinatorial contribution to the excess Gibbs energy in the UNIQUAC equation to obtain better representation of systems with a negligible residual contribution to the Gibbs energy as well as infinite dilution activity coefficients.

The number of modifications made to the UNIQUAC equation is perhaps indicative of its flexibility and suitability for application to describe equilibria in chemical processes. An extensive data base of UNIQUAC parameters for vapour-liquid equilibria (Gmehling *et al.*, 1977) and liquid-liquid equilibria (Sørenson and Arlt, 1979, 1980) for a large number of systems exists with new applications constantly appearing (Ruiz and Gomez, 1986).

2.2.5 Group contribution models

Organic molecules which belong to a given homologous series contain varying numbers of the same kind of segments or groups (Kehiaian, 1983). Considering this, it may be assumed that interactions between molecules depend more on the groups than on the molecules to which they are attached. Thus, a solution may be represented as a mixture of the groups which make up the components of the solution, with the configurational and interaction energy of the individual groups representing the behavior of the solution. Such methods, termed group contribution methods, become more powerful when the number of components is significantly larger than the number of groups required to represent these components. (Reid *et al.*, 1977). Group contribution methods are able to represent an extremely large number of chemical species with a much smaller number of groups and consequently, a significantly smaller number of fitted parameters. An underlying assumption of such models is that the groups which make-up the molecules of the solution components are independent from one another and thus their interaction energies do not depend on neighbouring groups (Fredenslund and Rasmussen, 1986). In addition to having the ability of representing a large number of systems based on fewer parameters, group contribution models provide a method to predict the behavior of systems for which little or no experimental data exist (Rasmussen and Fredenslund, 1978).

Derr and Deal (1969) proposed a model based on group contributions, which they call the ASOG (Analytical Solution of Groups) equation. This method combines a Flory-Huggins type expression for the combinatorial part of the activity coefficient with the Wilson equation adapted as a group contribution method, representing the enthalpic or residual contribution to the activity coefficient. This method has been modified by a number of authors for the representation of vapour-liquid equilibria. (Acree, 1984).

The UNIFAC model is a group contribution model originally developed by Fredenslund *et al.* (1975, 1977), based on the UNIQUAC equation. UNIFAC denoting the UNIQUAC functional activity coefficient. This model has been used to represent the vapour-liquid and liquid-liquid equilibria of a large number of systems (Fredenslund *et al.*, 1977).

Modifications have been made to the UNIFAC equation, many of which have been mentioned previously for application to the UNIQUAC equation (Kikic *et al.*, 1980; Alessi *et al.*, 1982; Skjold-Jørgensen *et al.*, 1980, 1981). Brandani and Prausnitz (1981) and Oishi and Prausnitz (1978) extended the UNIFAC equation with the inclusion of a free-volume term based on the work of Flory. This term represents the difference in free volume of a molecule in a solution compared to its pure liquid (Maurer and Prausnitz, 1978).

Data are now available for 43 groups with interaction parameters of many group pairs estimated in the 300-425 K temperature range. These data are all based on non-electrolyte systems (Fredenslund and Rasmussen, 1986). The UNIFAC model, with some modifications, has also been used to predict the enthalpies of mixing in a number of systems (Dang and Tasslos, 1986; Stathis and Tasslos, 1985).

Thomas and Eckert (1984) presented a group contribution model specifically developed for the prediction of activity coefficients at infinite dilution. This model is a significant improvement over UNIFAC for the prediction of 3357 experimentally available infinite dilution activity coefficients.

Fredenslund and Rasmussen (1985) presented a modified UNIFAC equation, which they call SuperFAC, that takes into account a number of the modifications made to the UNIQUAC/UNIFAC equations (Kikic *et al.*, 1980; Alessi *et al.*, 1982; Skjold-Jørgenson *et al.*, 1982). This model has been tested for the simultaneous representation of vapour-liquid and liquid-liquid equilibria and excess enthalpy over a wide temperature range on a fairly large number of systems. Six parameters are required per binary mixture. This model does a superior job correlating data when compared to the original equation. The model however, fails to predict the behavior of ternary solutions from binary data. The failure was partially a result of the inability to describe parameters representing association and solvation effects as group parameters. In addition, modifications made to the combinatorial contribution to the excess Gibbs energy resulted in unrealistic values for the infinite dilution activity coefficients of certain systems. This model has since been abandoned. (Fredenslund and Rasmussen, 1985).

A modified version of the UNIFAC equation has recently been presented (Fredenslund and Rasmussen, 1985) which has the ability to simultaneously represent both the excess enthalpy and the vapour-liquid equilibria of a number of systems. Simultaneous representation of liquid-liquid equilibria, however, is not good, although some improvement over the original UNIFAC equation is shown.

2.3 Aqueous Electrolyte Solutions

Due to the importance of water as an ionizing solvent and the ease of its experimental measurement, all but a very small part of the immense body of factual knowledge about electrolytes refers to aqueous solutions (Robinson and

Stokes, 1959). It is therefore not surprizing that the development of thermodynamically based models to predict the behavior of electrolytes has been based on aqueous systems.

2.3.1 The Debye-Hückel limiting law

The earliest relationship between the activity coefficient and the concentration of an aqueous electrolyte was presented by Lewis (Pitzer, 1984). He related the mean ion activity coefficient to the root of the molal ionic strength In 1923, Debye and Hückel published what would become one of the most significant advances in electrochemistry (Robinson and Stokes, 1959). In this theory, it was assumed that the non-ideality of solutions containing electrolytes was due only to the interionic forces between the dissociated ions. In the absence of these forces, an electrolyte solution would exhibit ideal behavior. To calculate the magnitude of the ionic interactions, Debye and Hückel simplified the complex charge distribution around a central ion to a time-averaged distribution. With this simplification, an estimate of the electrostatic potential at a central reference ion could be made and based on this, the excess Gibbs energy of the solution could be calculated. The charge distribution is assumed to be a spherically-symmetrical, radial Boltzman distribution (Robinson and Stokes, 1959; Harned and Owen, 1958). A modification to the theory was reported by Debye and Hückel who took into account the size of the ions. With this modification, the Debye-Hückel limiting law could be extended over a wider concentration range (Robinson and Stokes, 1959).

The Debye-Hückel limiting theory has been shown to be exact on statistical mechanical grounds in the dilute concentration range (Kirkwood and Poirer, 1954); this range being set as 0.001 molal ionic strength by Frank and Thompson (1959). Debye and Pauling (1925) showed that neither the variation of the dielectric constant in the immediate neighborhood of the ions, nor the deviation of the dielectric constant of the solution from that of the pure solvent has a significant effect on the limiting law for very dilute solutions of strong electrolytes. Güntelberg simplified the Debye-Hückel equation with the assumption that the ion size parameter, a_i, was constant and equal to 3 Å at all temperatures (Martin and Speakman, 1950).

2.3.2 Extensions to the Debye-Hückel theory

Guggenheim and Stokes (1969) extended the range of the Debye-Hückel limiting law by adding an extra term to the equation, linear in ionic strength. This term is based on Brønsted's concept of specific ion interaction (Brønsted, 1922), in which ionic interactions are assumed to be due only to interactions with ions of different sign. Ions of the same charge being uniformly influenced by all other ions of the same sign. With this new term, specific differences between individual electrolytes in a mixed solution could be accounted for without the introduction of any new parameters

(Horvath, 1985).

Robinson and Stokes (1959) extended the range of the Debye-Hückel equation by considering the effect of ionic strength and hydration and the resulting increase in net solute concentration due to this effect. Two parameters for a single electrolyte system are required: one representing the number of solvent molecules in the solvation shell and the second a new value for the distance of closest approach of the solvated ions. When both parameters are taken as constants, the solvation model gives good representation of the experimental results in aqueous solutions to an ionic strength up to 4 molal (Nesbitt, 1982). The limitations of this method are due primarily to the fact that the hydration number changes with ionic strength (Engles and Bosen, 1986). The extension of this method to multi-solute solutions requires a fixed solvation number be applied to specific ionic compounds. It has however, been shown that the solvation number is dependent on the nature of the companion ions in solution (Maurer, 1983).

Lietzke and Stoughton (1962) extended the range of the Debye-Hückel equation with a series expansion in terms of the solution molal ionic strength. They reported these parameters for a large number of aqueous electrolyte systems over a wide range of concentration. This method is not recommended for electrolytes which exhibit significant association (Liezke and Stoughton, 1972).

Meissner and Tester (1972) plotted the average ionic activity coefficient $(\gamma\pm^{(1/Z+\ Z-)})$ against the solution ionic strength in a number of aqueous strong electrolytes at 25°C and obtained a family of curves. Using these curves and a single value of the average ionic activity coefficient at 25°C, it is possible to estimate the variation of the activity coefficient over the entire concentration range. An equation to estimate the average, ionic activity coefficient of a number of electrolytes, based on a single parameter, has also been presented (Meissner *et al.*, 1972; Meisner and Kusik, 1979). Expressions accounting for the variation of the ionic activity coefficient with temperature (Meissner *et al.*, 1972; Meissner, 1980) and extending the treatment to mixed salt systems (Meissner, 1980; Meissner and Kusik, 1973) have also been presented.

A method to predict the mean activity coefficient of aqueous strong electrolytes to a molal ionic strength of 6 was given by Bromley (1973). The method is based on a single parameter (B) characteristic of the salt present. A method to approximate this parameter for any salt, based on its individual ions, was also presented. Parameters for 80 different ions were given. Perhaps the most significant application of the methods of Meissner *et al.* (1972) and Bromley (1973) is their use in systems for which no experimental data exist. The Bromley equation however, should not be used above a molal ionic strength of 6 (Horvath, 1985).

A number of other semi-empirical extensions to the Debye-Hückel equation have been published (Pytkowicz and Johnson, 1980; Pitzer, 1973), among which the method of Pitzer has become the most significant in industrial applications.

2.3.3 The Pitzer equation

Pitzer and coworkers (Pitzer, 1973; Pitzer *et al.*, 1977) developed an expression which, in addition to considering the interionic contribution to the non-ideality of aqueous strong electrolyte solutions through a modified Debye-Hückel term, also included the effects of short-range binary and ternary interactions between ionic species. The binary term is a function of the solution ionic strength, while the ternary term is independent of solution concentration. In single electrolyte systems, this equation is analogous to Brønsted's principle of specific ion interaction (Brønsted, 1922). The Pitzer parameters for many electrolyte systems have been tabulated by Pitzer and his colleagues at 25°C (Pitzer, 1973; Pitzer and Mayorga, 1973,1974) as well as for mixed electrolyte systems (Pitzer and Kim, 1974). Extensions of the Pitzer equation to higher temperatures and to systems of weak electrolytes have also been published (Silverster and Pitzer, 1977; Bradley and Pitzer, 1979). Fürst and Renon (1982) applied the Pitzer equation to a number of aqueous mixed-salt solutions with good results using five of the eight possible parameters.

Beutier and Renon (1978) and Edwards *et al.* (1978) extended the Pitzer equation for application to vapour-liquid equilibria of weak electrolyte solutions. In Beutier's extension, the excess Gibbs energy of the solution is assumed to be the sum of three contributions, corresponding to ion-ion, ion-molecule and molecule-molecule interactions. The ion-ion interactions are represented by a simplified version of Pitzer's equation (Beutier and Renon, 1978). The contributions from ion-molecule interactions are estimated by the Debye-McAulay electrostatic theory (Harned and Owen, 1958). This term gives the electric work required to transfer ions from a solution with a dielectric constant equivalent to that of the pure solvent to a solution with a dielectric constant equal to that of the salt solution. Molecular interactions between different molecules are ignored, but both binary and ternary interactions between molecular solutes are retained. Bromley's approximation of interaction parameters of salts as the sum of the individual ion interactions was also applied

Edwards *et al.* (1978) used the Pitzer binary interaction parameters to represent the ion-ion, ion-molecule and molecule-molecule interactions. Ternary and like-ion interactions and interactions between molecular solutes were neglected. Recently Koh and his colleagues (1985) applied Pitzer's equation to solutions of univalent, strong electrolytes in aqueous methanol solutions. The modifications required for this system however, were empirical and the estimated parameters specific to the selected system.

The Pitzer equations are used extensively to correlate the behavior of aqueous electrolyte solutions. They do however, have limitations which prevent its application to some systems, particularly in the high concentration range (Horvath, 1985). The Pitzer equation is semi-empirical in nature, containing virial type higher order parameters, with the relationship between these parameters not fully understood (Horvath, 1985). Brønsted's specific ion interaction principle has also been disproven (Pitzer, 1973) and thus, at high ionic strengths, interactions between ions of like charge cannot be neglected. Finally, the ternary ion-ion interaction parameters in the Pitzer equation are significant in systems of high ionic strength (Pitzer, 1973) and these terms may only be neglected in solutions of ionic strengths of less than 2 molal (Chen *et al.*, 1982).

2.3.4 Molecular contribution models

A number of models which hold the potential for application to solutions containing both ionic and non-ionic solutes have recently been proposed. These models have been given the name molecular contribution models because of their inclusion of a term or terms to represent the non-ionic interactions in solutions with electrolytes.

Chen *et al.* (1980) presented an equation for solutions containing both ionic and molecular solutes. In this work, the excess Gibbs energy of the solution is calculated as the sum of two contributions: long-range interionic forces, and short-range interactions. The long-range forces are given by Pitzer's modified Debye-Hückel expression (1980), while the short-range interactions are accounted for by use of the local composition concept adapted from the NRTL equation (Renon and Prausnitz, 1968) for non-electrolyte liquid mixtures. The model assumes like-ion repulsion and local neutrality in calculation of local composition. Two parameters per single electrolyte-single solvent system are required. Parameters for more than 100 binary systems have been published (Chen *et al.*, 1979; Chen *et al.*, 1980; Chen *et al.*, 1982). Recently the model has been applied to aqueous mixed electrolyte solutions (Chen and Evans, 1986) and mixed solvent/salt systems (Mock *et al.*, 1986). The model has also been applied to the prediction of solid-liquid equilibrium in aqueous electrolyte systems (Chen, 1986).

In a similar model proposed by Cruz and Renon (1978, 1979) for aqueous solutions of strong electrolytes, the short-range forces are again accounted for by the NRTL equation, with solvation theory as the basis for the determination of local composition. The solution non-ideality due to the ionic interactions is accounted for by a Debye-Hückel contribution plus a Debye-McAulay term to account for the change in the dielectric constant of the solvent due to the presence of the ions. This model has been applied to a number of aqueous, strong electrolyte solutions (Cruz and Renon, 1978) and a weak electrolyte system (Cruz and Renon, 1979).

Recently, the extended NRTL equation proposed by Cruz and Renon (1978) was modified by Ball *et al.* (1985a). In the new expression, the dielectric constant of the solution, originally calculated empirically, is estimated based on Pottel's expression, as a function of the physical properties of the solution and the ionic radii. The Pauling values for the ionic radii (Pauling, 1940) were used to represent the behavior of the ions in solution. The modified equation with two adjustable parameters per binary solution was compared to Chen's model (Chen *et al.*, 1982) and a two parameter version of Pitzer's equation (Pitzer, 1973), for their ability to predict the behavior of mixed-salt solutions. The parameters required by each model were fitted based on aqueous solutions of single, completely dissociated salts. The fitted parameters were then used to predict the behavior of mixed-salt solutions and the results compared. The Pitzer model was found to give the most accurate results for all systems. The modified form of Cruz and Renon's equation, however, gave superior results in systems containing ions with higher charge numbers.

Christensen and coworkers (1983) proposed a model for aqueous electrolyte systems based on an extension of the UNIQUAC equation (Abrams and Prausnitz, 1975; Maurer and Prausnitz, 1978). In this expression, long-range electrostatic interactions are represented by a Debye-Hückel term corrected empirically with a term, linear in molal ionic strength after the work of Brønsted (1922) and Guggenheim (Guggenheim, 1952; Guggenheim and Stokes, 1969). The short-range forces are given by the UNIQUAC equation applied to mixtures containing dissociated ions. The assumption of like-ion repulsion is achieved by assuming large values for the anion-anion and cation-cation interactions in the residual contribution to the UNIQUAC term.

For single, completely dissociated electrolyte solutions, the equation requires the estimation of three parameters. The equation has been applied to the correlation of the mean activity coefficient of the salts and water activity of a number of single and mixed salt solutions. Good results were obtained for solutions containing ten different ions.

2.4 Electrolytes in Mixed Solvent Systems

Many of the models for the thermodynamics of phase equilibria recently proposed are easily extended to systems containing both ionic and non-ionic solutes. Previous methods used to represent phase equilibria in mixed solvent, electrolyte systems, however, have not been as systematic (Mock *et al.*, 1986). The models are highly empirical, concerned primarily with the manipulation of vapour-liquid equilibria by the addition of salts to distillations of industrial importance (Furter and Cook, 1967; Furter, 1977).

2.4.1 Early theories

The first quantitative correlation of the salt effect on the vapour-liquid equilibria of two solvent, one electrolyte systems was proposed by Johnson and Furter (1960). In this correlation, the logarithm of the ratio of the relative volatility in the electrolyte solution to the relative volatility in a salt-free solution of the same solvent composition, is a linear function of the salt concentration. The correlation is given by a single parameter termed the salt-effect parameter. Later studies of the salt effect on vapour-liquid equilibrium have shown the salt-effect parameter to be dependent on both the salt and solvent compositions and to have a limited range of applicability (Merenda and Furter, 1971; Furter and Merenda, 1972; Jaques and Furter, 1974a,b; Burns and Furter, 1979).

2.4.2 Pseudo-binary methods

In the special binary method, mixed solvent/salt mixtures are assumed to be binary mixtures in which each component in the solution is a volatile component containing salt. The presence of the salt is treated implicitly through the modified properties of the special binary mixtures. This method was originally devised by Jaques and Furter (1972b), and was used to test the thermodynamic consistency of salt effect data on vapour-liquid equilibrium (Jaques, 1974; 1979). With the application of the Wilson equation, the special binary method has been used to correlate the vapour-liquid equilibria of alcohol-water mixtures saturated with salt (Jaques, 1976; Rousseau *et al.*, 1972).

Boone and coworkers (1976) presented a pseudo-binary method in which only one solvent component is modified with the addition of the salt; the second solvent component remains in its pure state. Activity coefficients derived using this approach are correlated using the Wilson equation (Boone *et al.*, 1976) and the UNIQUAC equation (Rousseau and Boone, 1978). Both these approaches give good results for many systems, however there is some question as to the thermodynamic consistency of the two methods (Sander *et al.*, 1986a).

2.4.3 Solvation methods

Ohe (1979) proposed a model for the prediction of vapour-liquid equilibria of mixed solvent, electrolyte systems based on the preferential solvation of the salt with one of the solvents in a two solvent system. The salt effect on the vapour-liquid equilibria is assumed to be due to this solvation effect, which effectively reduces the concentration of the solvent forming the preferential solvate. It must be assumed that the solvating molecules can not participate in the vapour-liquid equilibrium. This method has been used to describe systems containing calcium chloride, an alcohol and an ester (Ohe, 1979). The limitations of this method result from the inability to properly predict the solvation number. The solvation number is dependent on both the solvent and salt composition. In addition to this, systems which do not solvate preferentially with one of the solvent components cannot be treated in this way (Mock *et al.*, 1986).

2.4.4 Local composition methods

Hala (1983) reported an empirical method for the description of vapour-liquid equilibria in solutions of strong electrolytes in mixed solvents. In this method the Wilson equation is combined with an empirical term which accounts for the electrostatic interactions between the ions. Using this method, the vapour-liquid equilibria of ternary LiCl-methanol-water is described with good accuracy at 60°C from binary parameters.

Sander and coworkers (Sander *et al.*, 1986a,b,c) in some recently published work, presented an extended UNIQUAC equation for application to mixed solvent, electrolyte systems. In this model, short-range non-ionic interactions are represented by the UNIQUAC equation with the interionic interactions being described by the Debye-Hückel limiting law, modified empirically for application to mixed solvent systems. The model was used to correlate vapour-liquid equilibrium of 54 ternary data sets over a wide concentration range. It has also been applied to the vapour-liquid and solid-liquid equilibria of the nitric acid, water, nitrate salt system with good success. This method, however, has not been shown to have the ability to predict the ionic activity coefficients in any of these systems.

Results for the application of the Chen-NRTL model to mixed solvent systems have recently been published (Mock *et al.*, 1986). The model gave good results for the prediction of vapour-liquid equilibria in 47 single-solvent electrolyte systems and 33 mixed solvent/electrolyte systems and for the liquid-liquid equilibria of the mixed solvent electrolyte systems over a wide range of temperature and composition. The model requires nine adjustable parameters per binary solvent, single electrolyte system. Ionic activity coefficients in mixed solvent solutions cannot be represented by this model. In fact, the long-range interaction contribution was found to have little effect on the solvent behavior and was subsequently dropped prior to the parameter estimation procedure (Mock *et al.*, 1986). These parameters are fitted with vapour-liquid equilibria data of the solvent components only.

3. THERMODYNAMIC MODELLING OF FOOD SOLUTIONS

The thermodynamic modeling of phase equilibria in liquid systems has traditionally been approached from the standpoint of deviation from ideality through the use of thermodynamic excess functions. These functions describe the thermodynamic properties of real solutions which are in excess of those of an ideal solution under the same conditions. Excess enthalpy (H^E), excess Helmholtz energy (A^E) and excess Gibbs energy (G^E) are used to simplify the thermodynamic description of phase equilibria under different conditions of temperature, pressure and composition (Balzhiser *et al.*, 1972). The excess Gibbs function yields activity coefficients which give a quantitative measure of the departure from ideal behavior of individual components.

Most real solutions do not exhibit ideal behavior. The non-ideality may be due to structural effects, electrostatic interaction due to ions and natural and induced dipoles, non-polar interactions and chemical interactions. The behavior of solutions is therefore influenced by many different factors and to treat all aspects of the problem individually would result in a hopelessly complicated situation (Prausnitz *et al.*, 1986). To develop models for such a complex situation, it is necessary to ignore certain aspects of the physical situation which do not significantly affect the system behavior. Judicious choice of simplifying assumptions will result in models which realistically describe the behavior of a group of solutions under the assumptions retained for the model and are manageable from a practical point of view.

3.1 Statistical Thermodynamics

The link between the description of the sources of non-ideality on a molecular level and quantitative, numerical results is provided by concepts from statistical mechanics and molecular physics. Statistical mechanics attempts to describe the macroscopic behavior of systems in terms of microscopic properties. Statistical thermodynamics uses this approach to describe equilibrium states.

The thermodynamic specification of a macroscopic system provides only a partial and incomplete description from a molecular point of view. On a microscopic level, a measured property when viewed over a short time, is a fluctuating quantity. In practice however, the time required for a macroscopic measurement is sufficiently long that the fluctuations are not observed and the macroscopic property is a time-average of the many different quantum states that the system may assume (Prausnitz *et al.*, 1986). The object of statistical thermodynamics may therefore be stated as the calculation of these time-averaged quantities as a function of molecular properties.

A detailed discussion of statistical thermodynamics is not appropriate in this context. It is sufficient to note that molecular level descriptions of the sources of non-ideality in solutions are related to macroscopic thermodynamic quantities through statistical thermodynamics.

3.2 Modelling of the Excess Gibbs Energy

The Gibbs energy of a system describes the state of that system under conditions of constant temperature and pressure. Equilibrium of a closed system, under these conditions may be defined as a state in which the total Gibbs energy of the system is at a minimum with respect to all possible changes at a given temperature and pressure (Loncin and Merson, 1979). The Gibbs-Duhem equation defines the relationships between the thermodynamic and physical properties of a system in equilibrium and places restraints on the simultaneous variation of these properties in a single phase (Prausnitz *et al.*, 1986). Differentiation of the excess Gibbs energy with respect to composition, temperature and pressure yields respectively: the activity coefficient (γ_i) , the excess enthalpy (H^E) and excess volume (V^E) . Most liquid phase thermodynamic models involve the estimation of the excess Gibbs energy of a system through statistical thermodynamics (Renon and Prausnitz, 1978).

In many models the volume change accompanying the mixing of solution components is assumed to be zero. Small volume changes do have a significant effect on both the excess entropy and excess enthalpy of mixing but these effects tend to cancel in the excess Gibbs energy (Abrams and Prausnitz, 1975). With this assumption, the excess Gibbs energy (G^E) at constant temperature and pressure may be substituted for by the excess Helmholtz energy (A^E) at constant ~~temperatu~~re and volume. This substitution allows the developement of relatively simple, yet physically meaningful theories for this quantity.

3.2.1 Selection of a model for application to food solutions

Most solutions commonly found in food processing applications are aqueous in nature, containing a wide variety of components. The components which make up these multicomponent solutions may include: alcohols, carbohydrates, amino acids, salts and minerals, present as both free and associated ions. The complexity of such systems has been the major problem in the thermodynamic modelling of food systems. The model selected to represent food solutions must be applicable to many different types of components including both electrolytes and non-electrolytes and the extended UNIQUAC equation (Christensen *et al.*, 1983) holds the potential for such an application.

The extended UNIQUAC equation has been applied to aqueous solutions of single and mixed strong electrolytes over a fairly wide temperature and concentration range (Christensen *et al.*, 1983). In the absence of electrolytes, the equation reduces to the UNIQUAC equation (Abrams and Prausnitz, 1975; Maurer and Prausnitz, 1978). This equation has been used successfully to correlate liquid phase activity coefficients in a large number of systems, including polar-bonding systems such as aqueous ethanol (Anderson and Prausnitz, 1978a,b) and partly miscible systems such as the chloroform-water-acetone system (Abrams and Prausnitz, 1975). As a result of its wide use, there is a large data base of parameter values for components, of which many may be commonly found in food solutions (Prausnitz *et al.*, 1980; Gmehling *et al.*, 1977). The UNIQUAC equation has the added advantage of being based on binary parameters. Theoretically, the behavior of complex, multicomponent solutions may be predicted based only on data for binary systems. The UNIQUAC equation is used to represent the thermodynamic behavior of chemical systems in industrial applications. This in itself attests to the reliability of the model.

The extended UNIQUAC equation was selected to model the thermodynamic behavior of food solutions. It was selected for its flexibility in the treatment of both electrolytes and non-electrolytes and because of the large data base of parameter values for non-electrolyte systems available in the literature.

3.3 The Extended UNIQUAC Equation

The complexity of solutions containing electrolytes results from the many different phenomena occurring simultaneously in the mixture. These include long-range, electrostatic interactions between ions, solvation and association of ionic compounds, as well as short-range, dispersion and electrostatic forces between dipoles. This situation is made more complex when a mixed solvent is considered.

The extended UNIQUAC equation (Christensen *et al.*, 1983) is a model for the excess Gibbs energy of aqueous solutions of single and mixed electrolytes. It is semi-empirical in nature, accounting for contributions from the excess entropy and excess enthalpy of the solution to the excess Gibbs energy with separate terms. Recall that the excess Gibbs energy (G^E) is an operational combination of the excess entropy (S^E) and excess enthalpy (H^E):

$$G^E = H^E - TS^E \qquad [3.3.1]$$

The excess enthalpy is primarily concerned with energetic interactions, while the excess entropy considers the structure and spacial arrangement of the solution. A model for the excess Gibbs energy having physical significance should properly represent both the excess enthalpy and excess entropy individually, as these are physically significant quantities which can be related to molecular behavior (Prausnitz, 1977). The interactions which occur within the solutions depend on the structure of the solution and conversely, the structure of the solution is influenced by the interactions within. Although these effects are treated separately, they are interdependent.

In the extended UNIQUAC equation (eqn. 3.3.19), the contributions to the excess Gibbs energy due to the interactions between molecules and ions in the solution are separated into long-range ionic interactions and short-range interactions between all species. To represent the long-range interactions between ions, Christensen uses the Debye-Hückel limiting law. This term, however, is valid only in the dilute concentration range (Horvath, 1985). To account for these interactions beyond the dilute range, an empirical correction in the form of a virial term is added.

Short-range interactions and structural effects are accounted for using a local composition expression based on the UNIQUAC equation (Abrams and Prausnitz, 1975; Maurer and Prausnitz, 1978) which is adapted to solutions containing completely dissociated electrolytes. The total excess Gibbs energy of the solution is calculated as the sum of three terms:

$$G^E_{(total)} = G^E_{(ionic)} + G^E_{(residual)} + G^E_{(combinatorial)} \qquad [3.3.2]$$

Individual activity coefficients of the solution components are calculated by differentiation of the excess Gibbs function and application of the Gibbs-Duhem equation. The theoretical basis for each of the contributions to the excess Gibbs energy will be reviewed.

3.3.1 Electrostatic interactions

Electrostatic interactions are represented, in the extended UNIQUAC equation, by the Debye-Hükel limiting law (Robinson and Stokes, 1959), which for the unsymmetric molar excess Gibbs energy (G^{E*}) generalized to mixed solvents is given by:

$$\frac{G^{E*}_{DH}}{RT} = -\Sigma x_k \; M_k \; \frac{4A}{b^3} \left(\ln(1+b\sqrt{I}) - b\sqrt{I} + \frac{b^2 I}{2}\right) \qquad [3.3.3]$$

where A is a physical constant given by:

$$A = c \; \frac{\rho^{1.5}}{(\epsilon T)^{1.5}} \qquad [3.3.4]$$

Where:

$$c = 1.3287\times10^{5} \left[K^{1.5} \; m^{1.5} \; mol^{-.5}\right]$$

Where ρ is the density of the solvent mixture (kg m^{-3}), ϵ is the dielectric constant of the solvent mixture, and T is the system temperature (K). The ionic strength is given by $I = \frac{1}{2}\Sigma \; m_i Z_i^2$, where Z_i is the charge number of ion i and m_i the molality of ion i (mol kg $solvent^{-1}$) and b is a solution parameter which is a function of the ion size and solvent dielectric constant.

Christensen used a constant value of 1.5 for the value of b in aqueous solutions. Setting this value to a constant is equivalent to assuming that all the ions in solution have the same size and that the influence of the variation of the solvent dielectric constant on the value of b is small. In mixed solvents, the dielectric constant varies significantly with composition, thus for this term the theoretical expression is used. The parameter b is defined as follows (Robinson and Stokes, 1959):

$$b = \frac{2.184\times 10^{9}\ a^{\circ}}{(\epsilon T)^{1.5}} \left[K^{1.5} m^{-1}\right] \qquad [3.3.5]$$

For the ion size parameter (a°) a value of 4.53 x 10^{-8} m (Christensen *et al.*, 1983) is used for all ions. For details on the Debye-Huckel theory, the reader is refered to the monographs of Robinson and Stokes (1959) and Harned and Owen (1958).

By differentiation of equation 3.3.3 with respect to the mole fraction of a single ion, the rational unsymmetric activity coefficient (γ_i^*) of ion i, on a mole fraction basis is given by:

$$\ln\gamma^{*\,DH}_{i} = -Z_i\ A\ \frac{\sqrt{I}}{1+b\sqrt{I}} \qquad [3.3.6]$$

The unsymmetric excess Gibbs function (G^{E*}) is related to the symmetric Gibbs function (G^{E}) as follows:

$$\frac{G^{E*}}{RT} = \frac{G^{E}}{RT} - \Sigma x_i\ \ln\ \gamma_i^{\infty} x_i^{\infty} \qquad [3.3.7]$$

where γ_i^{∞} is the infinite dilution activity coefficient of ion i (i.e. $\Sigma x_i \rightarrow 0$ for all ions.) (See Appendix 2)

For a solvent component, the contribution to the symmetric activity coefficient (γ_s) from the Debye-Hückel limiting law is:

$$\ln\gamma_s^{DH} = M_s \frac{2A}{b^3}\left(1+b\sqrt{I} - \frac{1}{(1+b\sqrt{I})} - 2\ln(1+b\sqrt{I})\right) \qquad [3.3.8]$$

where M_s is the molecular weight of solvent s (kg mol^{-1})

To account for the electrostatic interactions beyond the theoretical range of the Debye-Hückel limiting law, an empirical, virial term is added. This term is similar to the empirical term used by Guggenheim (1952) to extend the range of the Debye-Hückel limiting law. For the unsymmetric Gibbs energy it has the following form:

$$\frac{G^{E*}_{BG}}{RT} = \Sigma x_k\ M_k\ \Sigma_a \Sigma_c\ \frac{\beta_{ac}}{T}\ m'_a m'_c \qquad [3.3.9]$$

where β_{ac} is a parameter representing the interaction between anion a and cation c. In the definition of β, Brønsted's theory of specific ion interactions (Brønsted, 1922) is applied. Activity coefficients depend only upon the actions of ions of opposite sign and the nature of the solvent. This interaction is represented by the parameter β, which is a function of solvent composition. The contributions to the rational, unsymmetric activity coefficients of individual ions from this empirical term are given for a cation as:

$$\ln\gamma^{*}{}_c{}^{BG} = \Sigma_a\ \frac{\beta_{ac}}{T}\ m'_a \qquad [3.3.10]$$

and for an anion:

$$\ln \gamma^{*}{}_a^{BG} = \Sigma_c \frac{\beta_{ac}}{T} m'_c \qquad [3.3.11]$$

where m_a and m_c are the molalities of anion a and cation c. For a solvent component, the contribution to the symmetric activity coefficient is given by:

$$\ln\gamma_s^{BG} = - M_s \Sigma_c\Sigma_a \frac{\beta_{ac}}{T} m'_a m'_c \qquad [3.3.12]$$

where the summations, Σ_a and Σ_c are over all anions and cations. One of the limitations of this approach, accounting for electrostatic interactions, is the treatment of the ions as a "smeared out" cloud of spherical, symmetric charge. Above the limit of infinite dilution, ions in solution behave more as discrete point charges. This results in large fluctuations of the local electrostatic potential with time. For a more accurate description of electrolyte solutions at concentrations above the limiting Debye-Hückel concentration, these factors must be taken into account (Pitzer, 1977).

3.3.2 UNIQUAC equation

Solution non-ideality due to electrostatic interactions has been accounted for with the Debye-Hückel and Brønsted-Guggenheim terms. To account for the spatial or structural effect and the short-range, non-ionic interactions, Christensen *et al.* (1983) used the UNIQUAC equation(Abrams and Prausnitz, (1975); Maurer and Prausnitz, (1978)). The UNIQUAC equation is a semi-empirical representation of the excess Gibbs energy of solutions based on Guggenheim's quasi-chemical treatment. Guggenheim's treatment is restricted to non-random mixtures of uniform size; in the UNIQUAC equation this analysis is extended to solutions containing molecules of different sizes.

The UNIQUAC equation consists of two terms : a residual term and a combinatorial term. The residual term represents the contribution to the excess Gibbs energy due to the intermolecular forces. In solutions of strongly interacting molecules, there are large deviations from random mixing, and these deviations have a significant effect on the assessment of the molecular interactions. To account for the effect of non-randomness, the UNIQUAC equation uses Wilson's local composition concept (Wilson, 1964).

This theory may be summarized as follows: solutions of non-homogenous molecules have a preference for choosing their immediate environment. This results in regions or domains of different compositions within a single solution. This effect, however, cannot be directly related to the overall composition. In Wilson's model, it is assumed that the local composition can be related to the overall composition through Boltzman factors. The concentration of a molecule i, in the immediate environment around a central molecule j, depends upon the strength of the interaction between the two different molecules relative to the interaction between two molecules of component j. If the strength of these interactions is uniform, the local composition is equal to the stoichiometric composition.

In the UNIQUAC equation, only interactions between molecules and their nearest neighbours are considered to be significant. The excess Gibbs energy, due to these interactions is assumed to be proportional to the relative surface area fraction of each component. This term contains two adjustable binary parameters and relates to the excess enthalpy of mixing of the solution.

The UNIQUAC combinatorial term describes the entropic contribution to the excess Gibbs energy. This term is required as a boundary condition at the limit of very high temperature. Under such conditions, the solution is athermal. The Staverman-Guggenheim equation was selected by Abrams and Prausnitz (1975) to represent this condition. This equation accounts for variations in the size and shape of the molecules which make up the mixture and depends only on parameters representative of the volume and surface area of the molecules in solution. To estimate these parameters, pure component data based on the crystal structure of the molecules are used (Abrams and Prausnitz, 1975). The complete UNIQUAC equation is given below:

$$G^E_{(UNIQUAC)} = G^E_{(residual)} + G^E_{(combinatorial)} \qquad [3.3.13]$$

such that:

$$\frac{G^E_{(combinatorial)}}{RT} = \Sigma x_i \ \ln \frac{\phi_i}{x_i} + \frac{z}{2} \ \Sigma q_i x_i \ln \frac{\theta_i}{\phi_i} \qquad [3.3.14]$$

and:

$$\frac{G^E_{(residual)}}{RT} = -\Sigma q_i x_i \ \ln \ (\Sigma_j \ \theta_j \ \tau_{ij}) \qquad [3.3.15]$$

Where:

$\phi_i = \frac{r_i x_i}{\Sigma_j \ r_j x_j}$ = Component volume fraction

$\theta_i = \frac{q_i x_i}{\Sigma_j q_j x_j}$ = Component surface area fraction

$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$

x_i = mole fraction of component i

q_i = pure component surface area parameter

r_i = pure component volume parameter

z = coordination number, set equal to 10

and:

$$\tau_{ij} = \exp -\left[\frac{U_{ij} - U_{jj}}{T}\right]$$

where:

U_{ij} = parameter representing the potential energy of interaction between molecules i and j.

T = temperature (K)

The coordination number (z) is representative of the number of nearest neighbours in the lattice structure. This value may range from 6-12, depending on the type of packing in the system lattice. Empirically, for typical liquids under ordinary conditions (i.e. normal temperature and pressure), z is close to 10 (Prausnitz *et al.*, 1986).

To obtain individual component activity coefficients on a symmetric basis in which the standard state is the pure liquid (See Appendix 2), the excess Gibbs function is differentiated with respect to the individual components.

$$RT \ln \gamma_i = \left.\frac{\partial G^E}{\partial n_i}\right]_{T,P,n_{j \neq i}} \qquad [3.3.16]$$

From the UNIQUAC equation, the individual symmetric activity coefficients are calculated as:

$$\ln\gamma_i^{UNI} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\phi_i} + l_i \frac{\phi_i}{x_i} \Sigma_j x_j l_j$$

$$- q_i \ln (\Sigma_j \theta_j \tau_{ji}) + q_i - q_i \Sigma_j \frac{\theta_j \tau_{ij}}{\Sigma_k \theta_k \tau_{kj}} \qquad [3.3.17]$$

Ion activity coefficients are expressed on an unsymmetric basis with their reference state being the infinitely dilute solution (See Appendix 2). Activity coefficients normalized in this way are calculated from the UNIQUAC equation as follows:

$$\ln \gamma_i^{UNI,*} = \ln\gamma_i^{UNI,x} - \ln\gamma_i^{UNI,\infty} \qquad [3.3.18]$$

where $\gamma_i^{UNI,x}$ is UNIQUAC symmetric activity coefficient at the solution composition and $\gamma_i^{UNI,\infty}$ is the UNIQUAC activity coefficient in the infinitely dilute reference state. Both these quantities are calculated using equation 3.3.17.

For the structural parameters, q_k and r_k the van der Waals volume and surface areas, normalized to a standard segment are used. The van der Waals volumes and surface areas used are those given by Bondi (1968). The normalization of these values with respect to a standard segment is arbitrary and, for this, Abrams and Prausnitz (1975) used the volume and surface area of a single methylene group in a polyethylene molecule calculated using the van der Waals volume and area parameters. For details on the UNIQUAC equation, the reader is referred to the derivations by Abrams and Prausnitz (1975) and Maurer and Prausnitz (1978).

For molecules of uniform size and shape the UNIQUAC equation reduces to the Wilson equation (Maurer and Prausnitz, 1978). In mixtures of non-polar components for which the interactions between the molecules can be assumed to be uniform, the equation reduces to the Staverman-Guggenheim expression.

To adapt this equation to solutions containing dissociated ions, the individual ions must be treated as independent species. Mole fractions must also be calculated, treating the ions in this way (See Appendix 1).

In Christensen's extended UNIQUAC model, the original UNIQUAC equation was used although, during the past decade numerous modifications of the equation have been made (Anderson and Prausnitz, 1978a,b; Kikic *et al.*, 1980;

Skjold-Jørgensen *et al.*, 1982; Alessi *et al.*, 1982). To account for like-ion repulsion effects within the solution (Chen *et al.*, 1982), the potential-energy parameters (U_{ii}) representing the interactions between ions of like-charge are arbitrarily set to a value of 5000 K (Christensen *et al.*,1983).

In summary, the extended UNIQUAC equation assumes the excess Gibbs energy function to be the sum of contributions from three terms: the Debye-Huckel limiting law representing long-range ionic interactions, a Brønsted-Guggenheim virial term and the UNIQUAC equation. The individual component activity coefficients are calculated as the sum of the partial molar excess Gibbs energies from each of these terms. For solvent components, the activity coefficient is calculated as :

$$
\begin{aligned}
\ln\gamma_s &= \ln \gamma_s^{UNI} \\
&\quad + M_s \frac{2A}{b^3}\left(1+b\sqrt{I} - \frac{1}{(1+b\sqrt{I})} - 2\ln(1+\sqrt{I})\right) \\
&\quad - M_s \Sigma_a \Sigma_c \frac{\beta_{ac}}{T} m'_a \, m'_c \qquad [3.3.19]
\end{aligned}
$$

For ions on an unsymmetric basis, the mole fraction-based activity coefficient is calculated from:

$$\ln\gamma_i^{*} = \ln \gamma_i^{UNI,x} - \ln \gamma_i^{UNI,\infty}$$

$$- z_i A \frac{\sqrt{I}}{1+b\sqrt{I}}$$

$$+ \Sigma_j \frac{\beta_{ij}}{T} m'_j \qquad [3.3.20]$$

The subscripts i and j refer to ions of opposite sign.

The equation has been used to represent the thermodynamic bahavior of a number of single and mixed-strong electrolytes in aqueous solution, with good results (Christensen *et al.*, 1983). In this study, the thermodynamic behavior of a representative food solution is modelled using this equation.

4. THERMODYNAMIC REPRESENTATION OF FOOD SOLUTIONS WITH THE EXTENDED UNIQUAC EQUATION

The engineering design and simulation of food processing operations requires a thermodynamically based representation of food systems. Most food solutions are very complicated mixtures and to account for all interactions occuring in these solutions would result in a model of such complexity, and requiring so many parameters, that its use for engineering purposes would be impractical. The approach normally taken in cases in which the reality of the situation is much more complex than our physical understanding, is the use of a simplified system. Food systems may be represented by model solutions in which only the essential elements are included. For example, to represent the behavior of orange and apple juices, Heiss and Schachinger (1949) used aqueous mixtures of the component sugars. Rüegg and Blanc (1981) modelled the behavior of honey with aqueous mixtures of sugars reflecting its carbohydrate composition. Present knowledge in the field of solution thermodynamics is limited to relatively simple chemical compounds. The solution thermodynamics of complex molecule such as proteins and enzymes however, is still in its infancy.

The amenability of the extended UNIQUAC equation to the modelling of food solutions will be tested using a simplified model food solution.

4.1 Selection of a Representative Food System

The food solution selected to validate the extended UNIQUAC equation was chosen in coordination with work presently under way on a Dehydrocooling process (LeMaguer and Biswal, 1984) A process motivated by the work of Robertson and Cippoletti (Robertson *et al.*, 1976; Cippoletti *et al.*, 1977) on the immersion freezing of vegetables using an aqueous freezant, Dehydrocooling is a process of simultaneous cooling and osmotic dehydration of plant tissue by direct contact with aqueous solutions of sodium chloride, ethanol and/or sucrose. The process is envisioned as a pretreatment to conventional freezing or drying techniques which improves the efficiency of these processes (Le Maguer and Biswal, 1984). There is also some indication that the process has beneficial effects on the organoleptic quality of the final product (Biswal and Le Maguer, 1986).

The engineering design of the Dehydrocooling process requires the representation of the mass tranfer phenomena occuring within plant tissue. Recent work by Toupin (1986) on the representation of cellular mass transfer using irreversible thermodynamics has been applied by Guenneugues(1986) to the modelling of osmotic dehydration of carrot tissue. Details of this work are given in Section 5.4.

The solution selected to test the validity of the application of the extended UNIQUAC equation to food systems is an aqueous solution of ethanol, sucrose and sodium chloride. Aside from its application to the design of the Dehydrocooling process, the selected solution contains components commonly found in food systems. It is a good representation of a simple food solution containing an electrolyte, carbohydrate and aroma compound.

4.2 Modifications to the Extended UNIQUAC Equation

In the application of the extended UNIQUAC equation to aqueous electrolyte solutions (Christensen *et al.*, 1983), there is no ambiguity in the classification of components as ionic solutes or—solvents. With the addition of non-ionic components to the system, this classification is not as clear.

In the representative food solution, all non-ionic species, including molecular solutes, are classified as solvent components. This definition is used in the calculation of the ion molalities required in the Debye-Hückel limiting law (equation 3.3.3); properties of the solvent are also calculated on this basis. (See Appendix 3).

The Brønsted-Guggenheim term requires ion concentrations on a molality basis. This term is empirical with no theoretical basis for the definition of the solvent. Based on a preliminary investigation, a new concentration variable was introduced. The ion concentrations were expressed in terms of moles of ion per kilogram of water in the solution. This term is defined as the aqueous molality and is calculated as follows:

$$m'_i = \frac{\text{moles ion i}}{\text{kg water}} \qquad [4.2.1]$$

With the introduction of this concentration variable, the Brønsted-Guggenheim specific-ion interaction parameter (β) can be expressed as a linear function of the solvent composition. The use of molalites based on the solvent require a higher order functionality to correlate β with the solvent composition. This non-linearity is most significant in solutions containing sucrose, due to the high molecular weight of sucrose compared to the other solvent components.

The specific-ion interaction parameter is calculated in the ternary systems using the following formula:

$$\beta = \beta_0 + B_{solv} W_{solv} \qquad [4.2.2]$$

where β is the specific-ion interaction parameter at the given solvent composition, β_0 is the specific-ion interaction parameter in aqueous solution, B_{solv} is the Brønsted-Guggenheim solvent parameter, giving the variation of β with the solvent weight fraction and W_{solv} is the weight fraction solvent (salt-free). This functionality is similar to one used by Koh *et al.* (1985) who correlated the parameters in the Pitzer equation (Pitzer, 1973) with the salt-free methanol weight fraction, in solutions of strong electrolytes in aqueous methanol.

For the calculation of the specific-ion interaction parameter in solutions containing a ternary solvent, a mixing rule based on the solvent composition and the value of β in the component binary systems has been developed. (See Section 5.1.)

4.3 Parameter Estimation

The popularity the UNIQUAC equation lies in its ability to predict the behavior of multicomponent solutions based on binary parameters. When the equation is extended to include electrolytes, this property no longer holds as the specific-ion interaction parameter (β) is a function of the ions present and the solvent composition. The variation of β must be estimated from ternary data.

Many components important in food systems have been studied using the UNIQUAC equation. Parameter values available in the literature for the model food system, will be used in this study. Binary parameters not available and ternary parameters will be estimated from experimental data on the appropriate system.

4.4 Optimization Procedure

The parameter optimizations performed in this work were performed using a procedure based on a modified Simplex technique. The procedure was adapted by Toupin (1986) from a search method developed by Nelder and Mead (1965a,b). This technique is an extension of the Simplex method introduced by Spendly and his colleagues (Spendly *et al.*, 1962). The Simplex search technique is a least squares, derivativefree, direct search method for the estimation of non-linear parameters. The objective function in this procedure is a weighted Chi-square statistic (χ^2), based on the deviation between the values predicted with the given model and the true value, usually based on experimental data. It is calculated in the following way:

$$\chi^2 = \sum_i w_i \left[Y_i^{Expt.} - Y_i^{Pred.} \right]^2 \qquad [4.4.1]$$

where $Y_i^{Expt.}$ is the experimental or true value of data point i; $Y_i^{Pred.}$ is the value of Y_i predicted using the model; and w_i is a weighting parameter representative of the confidence level or significance of the specified data point.

The weighting parameters are included in the calculation to take into account the experimental errors. This ensures that the resulting Chi-square statistic is representative of the quality of the experimental data (Toupin, 1986). A detailed description and explanation of the modified Simplex algorithm, including a listing of the computer programme used is available from Toupin (1986).

4.5 Binary Systems

A number of the binary systems which make-up the model food solution have been studied previously. The thermodynamic behavior of the aqueous sodium chloride and aqueous ethanol systems have been correlated using the extended UNIQUAC and UNIQUAC equations, respectively

(Prausnitz *et al.*, 1980; Christensen *et al.*, 1983). The parameters presented for these systems will be used in the application of the extended UNIQUAC equation to the sodium chloride-sucrose-ethanol-water system.

4.5.1 Aqueous sodium chloride solutions

In the original presentation of the extended UNIQUAC equation, Christensen and his coworkers (1983) correlated activity coefficients of aqueous solutions of single and mixed strong electrolytes. Included among these was the aqueous sodium chloride system. This system was fitted to a salt concentration of 11 molal and over a temperature range of 25-100°C. The volume (r_k) and surface area (q_k) parameters used for the water molecule were from Abrams and Prausnitz (1975). The Pauling ionic radii (Pauling, 1940) were used to calculate these parameters for the ions (Christensen *et al.*, 1983). The UNIQUAC interaction parameters (U_{ij}) representing the interaction between the water molecule and each ion and Brønsted-Guggenheim specific-ion interaction parameter (β) for the interaction between the sodium and chloride ions in pure water presented in this study will be used. These values are summarized in Tables 4.1, 4.2 and 4.3.

4.5.2 Aqueous ethanol solutions

The vapour-liquid equilibria of the aqueous ethanol system have been correlated using the UNIQUAC equation by a number of authors. The parameters used in these studies are given in a number of data compilations (Gmehling *et al.*, 1977; Prausnitz *et al.*, 1980). In these studies, the Bondi based surface area and volume parameters are used. Anderson and Prausnitz (1978a,b) used the UNIQUAC equation for the simultaneous representation of vapour-liquid and liquid-liquid phase equilibria of aqueous ethanol solutions. To yield better results, Anderson and Prausnitz modified the surface area parameters (q_k) of both the ethanol and water molecules used in the residual term of the UNIQUAC equation. These modified values were estimated from experimental activity coefficient data with no theoretical justification.

The use of these parameters in the extended UNIQUAC equation would require the reoptimization of the parameter values for the aqueous sodium chloride system, because these parameters were optimized based on the Bondi geometric (q_k,r_k) parameters of the water molecule. The Bondi based surface area parameter for the water molecule was therefore used in this study.

UNIQUAC interaction parameters for the aqueous ethanol system recommended by Prausnitz (Prausnitz *et al.*, 1980) are used in this work. These parameters were estimated based on a number of experimental studies. The ethanol surface area parameter (q_k) calculated from the van der Waals geometric parameters resulted in a better representation of the ethanol activity coefficient in ternary solutions of sodium chloride, ethanol and water and was selected for use in this study despite an inferior representation of aqueous ethanol solutions.

4.5.3 Aqueous sucrose solutions

The thermodynamic behavior of aqueous sucrose solutions has primarily been represented by simple empirical models based on extensive compilations of experimental data collected over many years of study. (Honig, 1953; Hugot, 1972). To the best of our knowledge, there has been no attempt to correlate the thermodynamic behavior of the sucrose-water system using the UNIQUAC equation.

The thermodynamic behavior of aqueous sucrose solutions has been reported by a number of researchers (Robinson and Stokes, 1959; Robinson and Stokes, 1961; Stroth and Schönert, 1977; Gucker *et al.*, 1939; Garrod and Herrington, 1970; Honig, 1953). A significant amount of data is available for this system. Most of the experimental data are in the form of water activities, expressed as osmotic coefficients or osmotic pressures and partial molar enthalpies. Sucrose activity coefficients may be calculated from the water activities using the Gibbs-Duhem equation. (See Appendix 4.)

The application of the extended UNIQUAC equation to this system involves only the UNIQUAC term as this system does not contain ionic solutes. Parameters representing the sucrose-sucrose and sucrose-water interactions are required. Volume (r_k) and surface area parameters (q_k) of the sucrose molecule must also be estimated. The parameter estimation procedure was performed based on the experimental data described previously. Estimates on the precision of the data were not available. It was therefore assumed that the % error on the experimental activity coefficients was uniform for all data. The parameter optimization was based on the minimization of a chi-square statistic based on the relative deviations of the activity coefficients:

$$\chi^2 = \Sigma\, w_i \left[\frac{\gamma_i^{exp} - \gamma_i^{pred}}{\gamma_i^{expt}}) \right]^2 \qquad [4.5.1]$$

The relative error on a given quantity is equivalent to the absolute error on the logarithm of that quantity. Using this property, the Chi-square statistic was calculated based on the absolute errors of the logarithm of the activity coefficients:

$$\chi^2 = \Sigma\, w_i \left[\ln\gamma_i^{exp} - \ln\gamma_i^{pred} \right]^2 \qquad [4.5.2]$$

In a preliminary study, the volume and surface area parameters of the sucrose molecule were calculated from the van der Waals parameters of the molecular groups which make up this molecule. For details on this procedure the reader is refered to the work of Choudhury (1987). The UNIQUAC interaction parameters (U_{ij}) were optimized with the Simplex procedure using activity coefficients of water and sucrose calculated from experimental data at 25°C (Robinson and

Stokes, 1959,1961). Good representation of the sucrose activity coefficient was obtained with the optimized parameters. The results are shown in Figure 4.1.

To test the validity of the estimated parameters, the partial molar excess enthalpies of sucrose at 25°C were calculated using the UNIQUAC equation. The estimated values were compared to the values calculated from the experimental data of Gucker *et al*. (1939) and Stroth and Schönert (1977). The predicted and experimental partial molar excess enthalpies of sucrose are shown in Figure 4.2. As illustrated, the UNIQUAC equation does not correctly predict the experimental behavior using the optimized interaction parameters. Proper prediction of the partial molar excess enthalpy is required if the variation of the activity coefficient with temperature is to be correctly estimated (Rasmussen, 1983).

Previous studies of the application of the UNIQUAC to non-electrolyte solutions have shown that the model may do a good job representing the excess Gibbs energy of the system; based on the same parameters, however, the prediction of the partial molar enthalpy is not good (Fredenslund and Rasmussen, 1985).

Although the Gibbs energy function is fitted properly with the UNIQUAC equation, the individual contributions do not correctly represent the individual entropic and enthalpic contributions (eqn 3.3.1). The proper representation of the total excess Gibbs energy results from

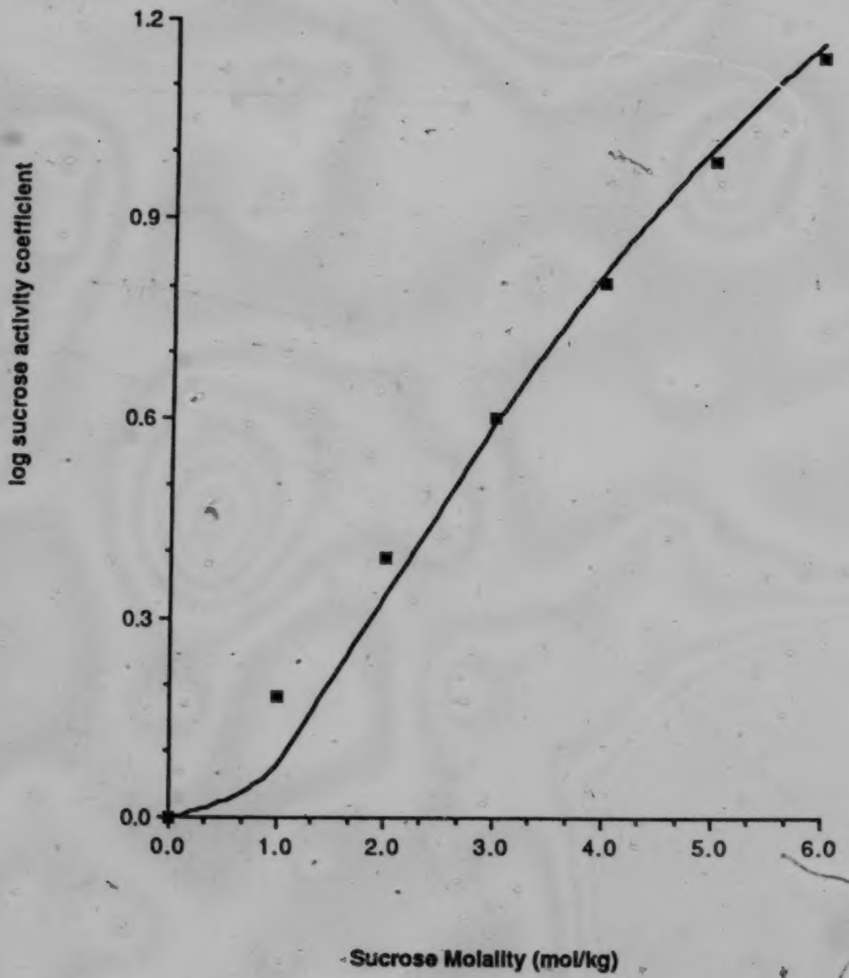

Figure 4.1 Predicted (-) and experimental (■) sucrose activity coefficient at 25°C. Experimental data adapted from Robinson and Stokes (1959,1961).

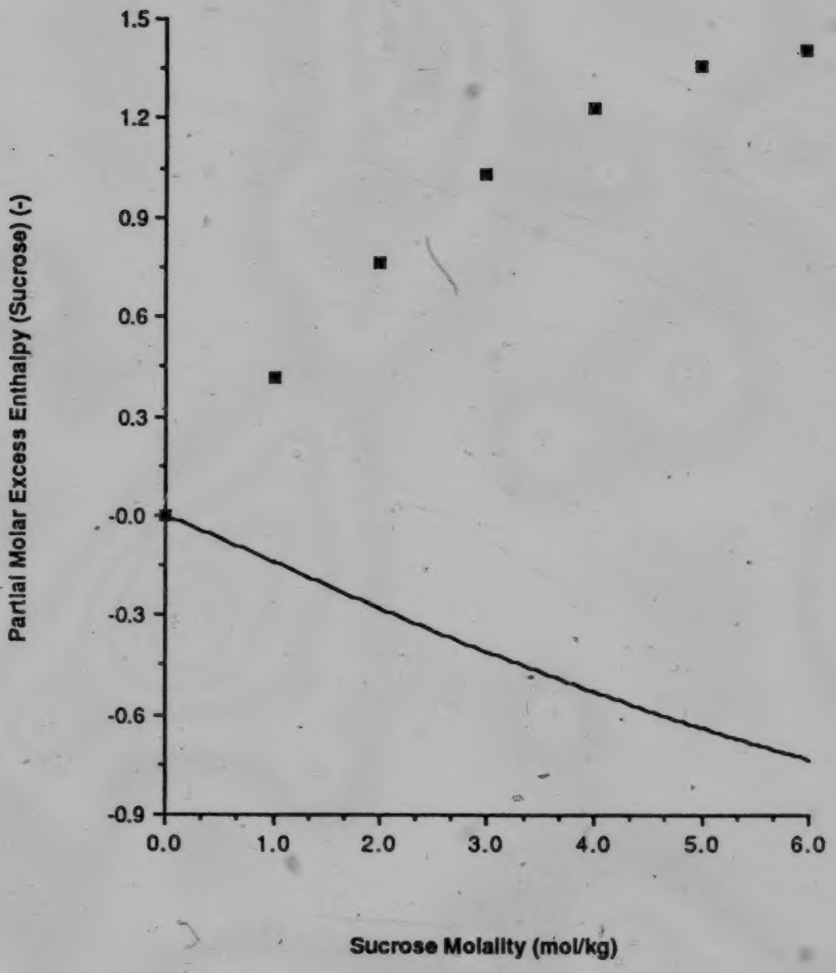

Figure 4.2 Predicted (-) and experimental (■) partial molar enthalpy ($\bar{h}^E/RT$) of sucrose at 25°C. Experimental data from Gucker *et al*. (1939) and Stroth and Schönert (1977).

fortuitous cancelling of the two contributions in this function (Fredenslund and Rasmussen, 1985).

The combinatorial term in the UNIQUAC equation represents the solution as an athermal mixture and depends only on volume (r_k) and surface area (q_k) parameters (Prausnitz *et al.*, 1986). Comparison of this term to experimental values of the partial molar excess entropy is indicative of the validity of these parameters. The partial molar entropies were calculated as shown in Appendix 4. As illustrated in Figure 4.3, the experimental values are not correctly represented.

Choudhury (1987) observed similar behavior in his study of the thermodynamic behavior of aqueous glucose solutions using the UNIFAC equation (Fredenslund *et al.*, 1977). To remedy this, he applied a free-volume correction (Oishi and Prausnitz, 1978), to account for the volume change in the solution which occurred upon mixing and modified the surface area parameter (q_k) of the hydroxyl group (OH) from the literature value. These modifications were empirical in nature.

The van der Waals parameters, used to estimate q_k and r_k in the UNIQUAC equation are based on x-ray diffraction and microwave data of molecular crystals (Bondi, 1968). It is assumed that the volume and surface area of any molecule, relative to the normalization factor, is the same in both the crystal and in solution. This assumption may be valid for non-polar or slightly polar mixtures such as

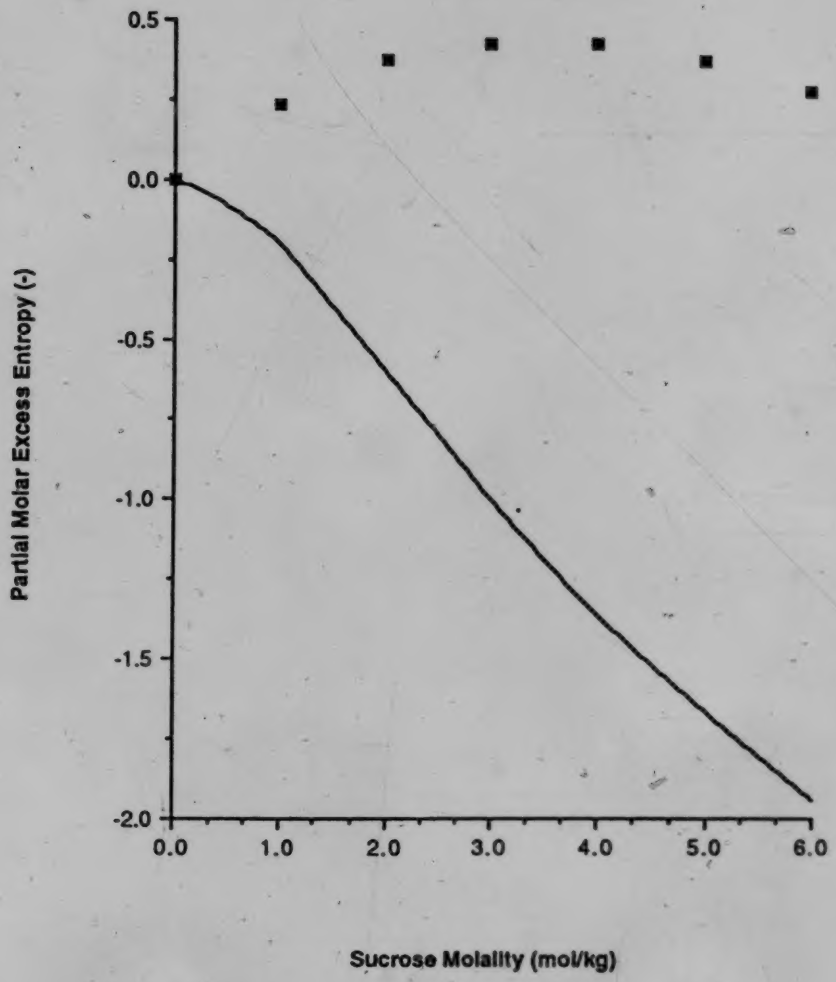

Figure 4.3 Predicted (-) and experimental (▪) partial molar entropy ($\bar{s}^E/R$) of sucrose at 25°C. Expt. data adapted from Robinson and Stokes (1959, 1961), Gucker *et al.* (1939) and Stroth and Schönert (1977).

hydrocarbons. For highly polar solutions of flexible molecules, such as aqueous sucrose, its validity may be suspect.

For a better representation of the partial molar excess entropies, and because these parameters control the behavior of the sucrose molecule in solution, the volume and surface area parameters of the sucrose molecule were estimated from the experimental partial molar entropies mentioned previously. The partial molar excess enthalpy and entropy are directly related to the logarithm of the activity coefficient and thus, the objective function used with these quantities is based on their absolute deviations.

The optimized parameters were found to be significantly smaller than those calculated with the Bondi parameters. (See Table 4.2.) The predicted and experimental reduced partial molar, excess entropies of sucrose and water using the optimized sucrose volume and surface area parameters are shown in Figure 4.4. With these parameters, the reduced, partial molar, excess entropies calculated from experimental data are represented well.

The reduction of the volume parameter agrees qualitatively with the findings of Kikic and his colleagues (1980) who proposed a modification in the combinatorial term of the UNIQUAC/UNIFAC equations. They proposed replacing the volume parameter r_k with $r_k^{2/3}$, effectively reducing the value of this parameter in the combinatorial term. Sander and his coworkers (1986a) in their modified UNIQUAC

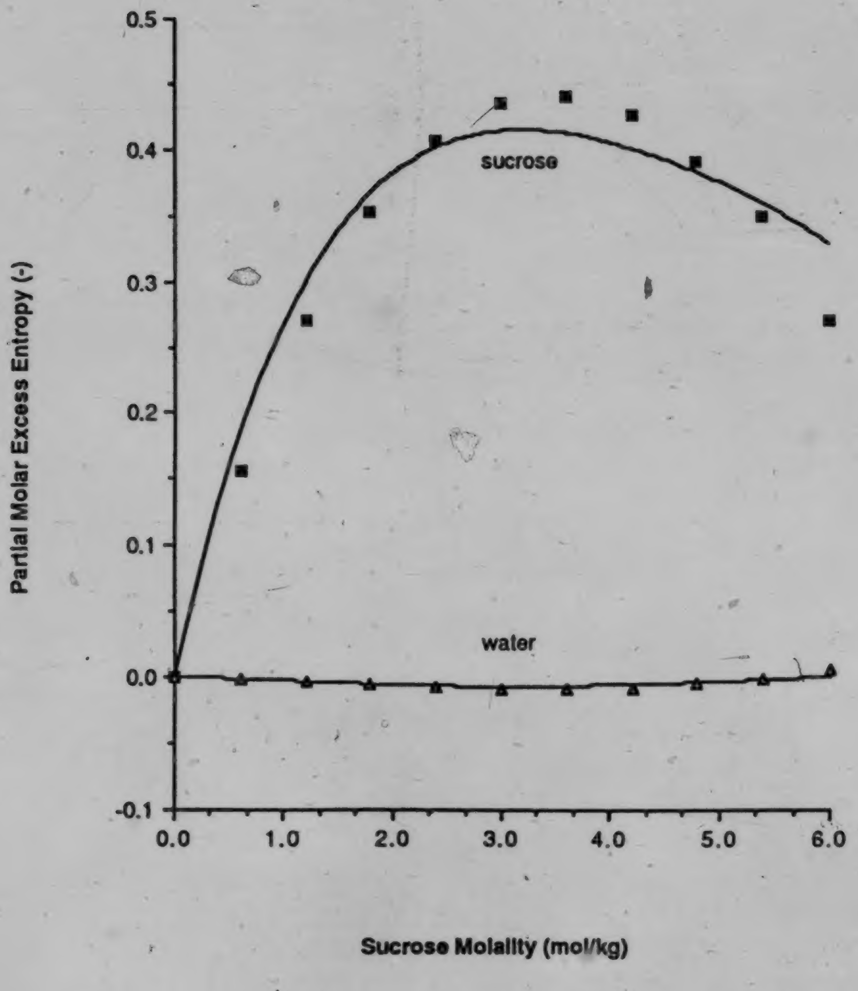

Figure 4.4 Predicted (-) and experimental partial molar entropies ($\bar{s}^E/R$) of sucrose (■) and water (Δ) Calculated with optimized q_k and r_k for sucrose

equation, made the volume and surface area parameters of all the cations, adjustable parameters.

Based on the optimized, geometric parameters for sucrose, the UNIQUAC interaction parameters (U_{ij}), were fitted with the experimental measurements of partial molar excess enthalpies at 20, 25 and 30° and activity coefficients at 0, 25, and 55.7°C. (See Appendix 4).

The parameters used for this system and the errors on the optimized parameters are summarized in Tables 4.1. and 4.2. The predicted and experimental partial molar excess enthalpies of sucrose and water at 25°C, are presented in Figure 4.5. The activity coefficients of sucrose and water predicted using the optimized parameters at 0, 25 and 55.7°C are given in Figures 4.6-4.8. Both the partial molar, excess enthalpies and activity coefficients in aqueous sucrose solutions are now predicted well.

The % residual mean square deviation (%RMSD) of the predicted and experimental activity coefficients is calculated using the following equation (Renon and Prausnitz, 1978):

$$\%\text{RMSD}\ \gamma = \sqrt{\left[\Sigma\ (\ln\gamma_i^{exp} - \ln\gamma_i^{pred})\right]^2/n}\ \times 100\% \qquad [4.5.3]$$

The average %RMSD of the activity coefficients in this system over the temperature and concentration range covered is 6.6%. The activity coefficients calculated with the estimated parameters are validated with the prediction of

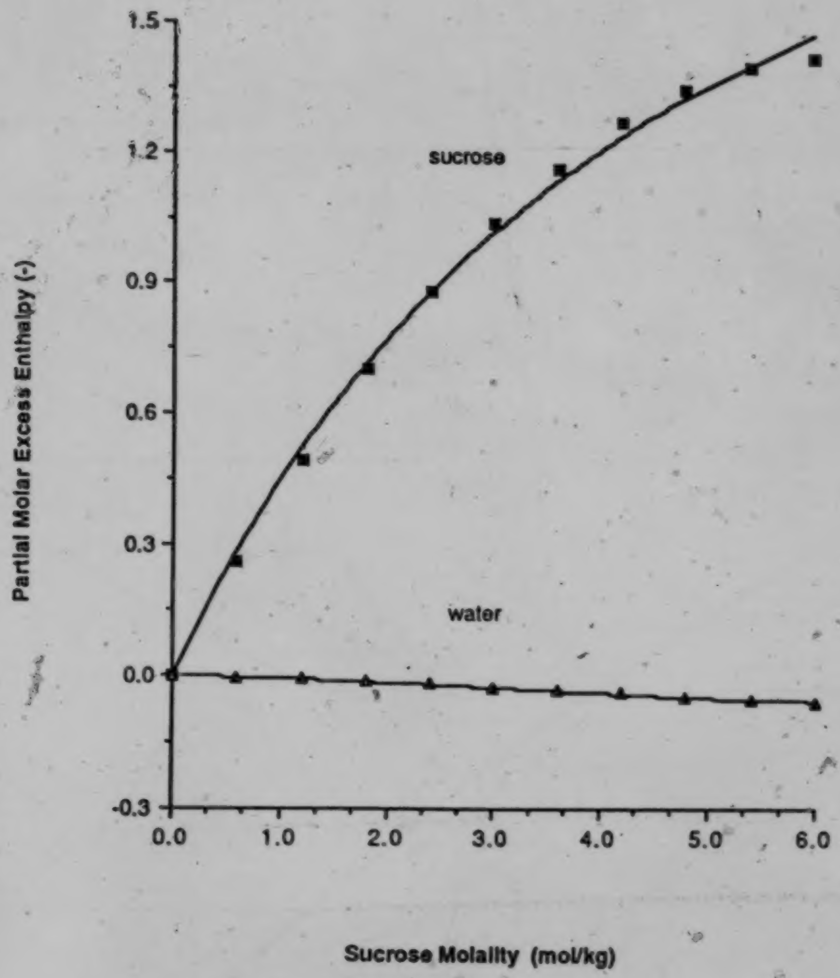

Figure 4.5 Predicted (-) and experimental partial molar enthalpy ($\bar{h}^E/RT$) at 25°C. Experimental data from Gucker *et al.* (1939). and Stroth and Schönert (1977).

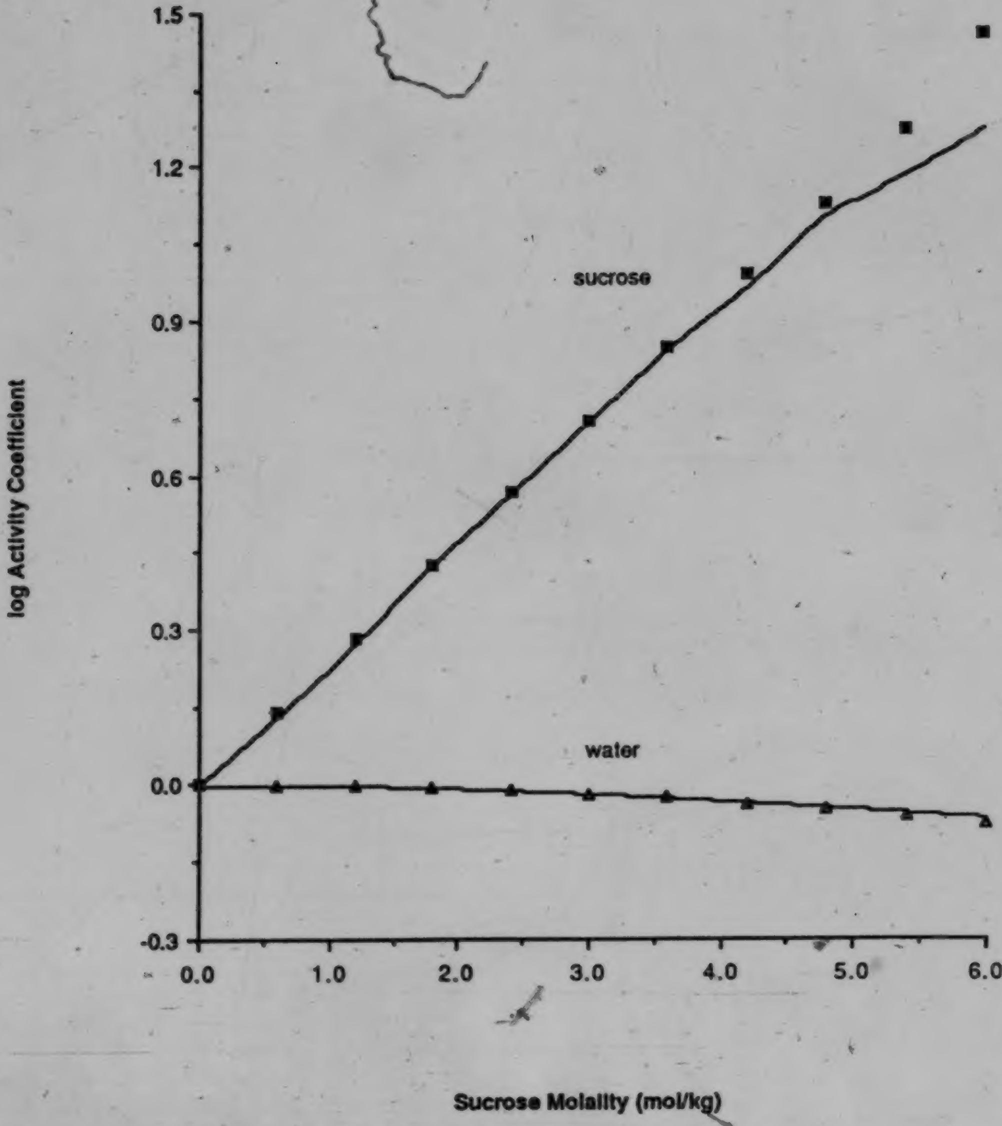

Figure 4.6 Predicted (-) and experimental sucrose (■) and water (Δ) activity coefficients at 0°C. Experimental data adapted from Honig (1953).

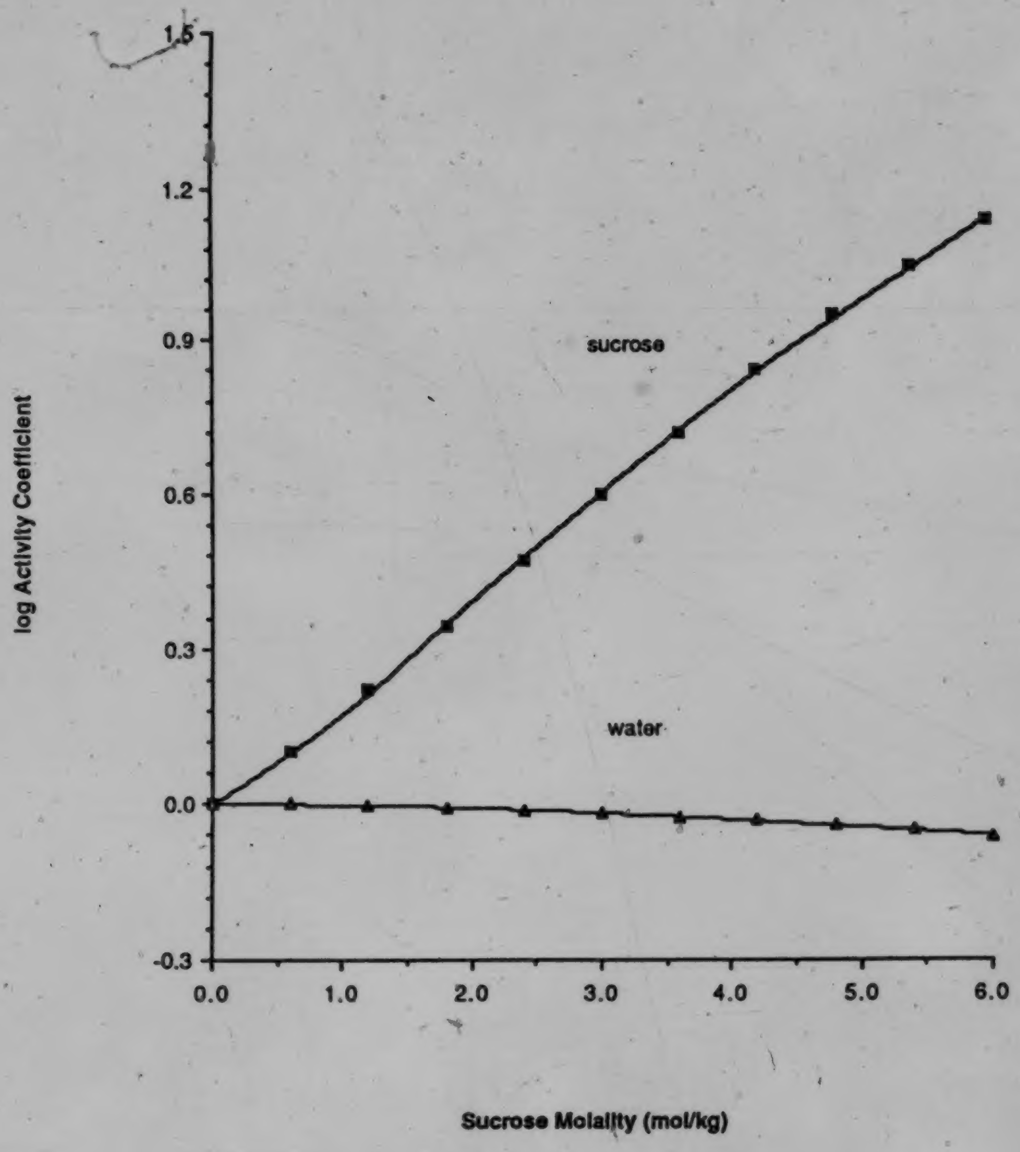

Figure 4.7 Predicted (-) and experimental sucrose (■) and water (Δ) activity coefficients at 25°C. Experimental data adapted from Robinson and Stokes (1959, 1961).

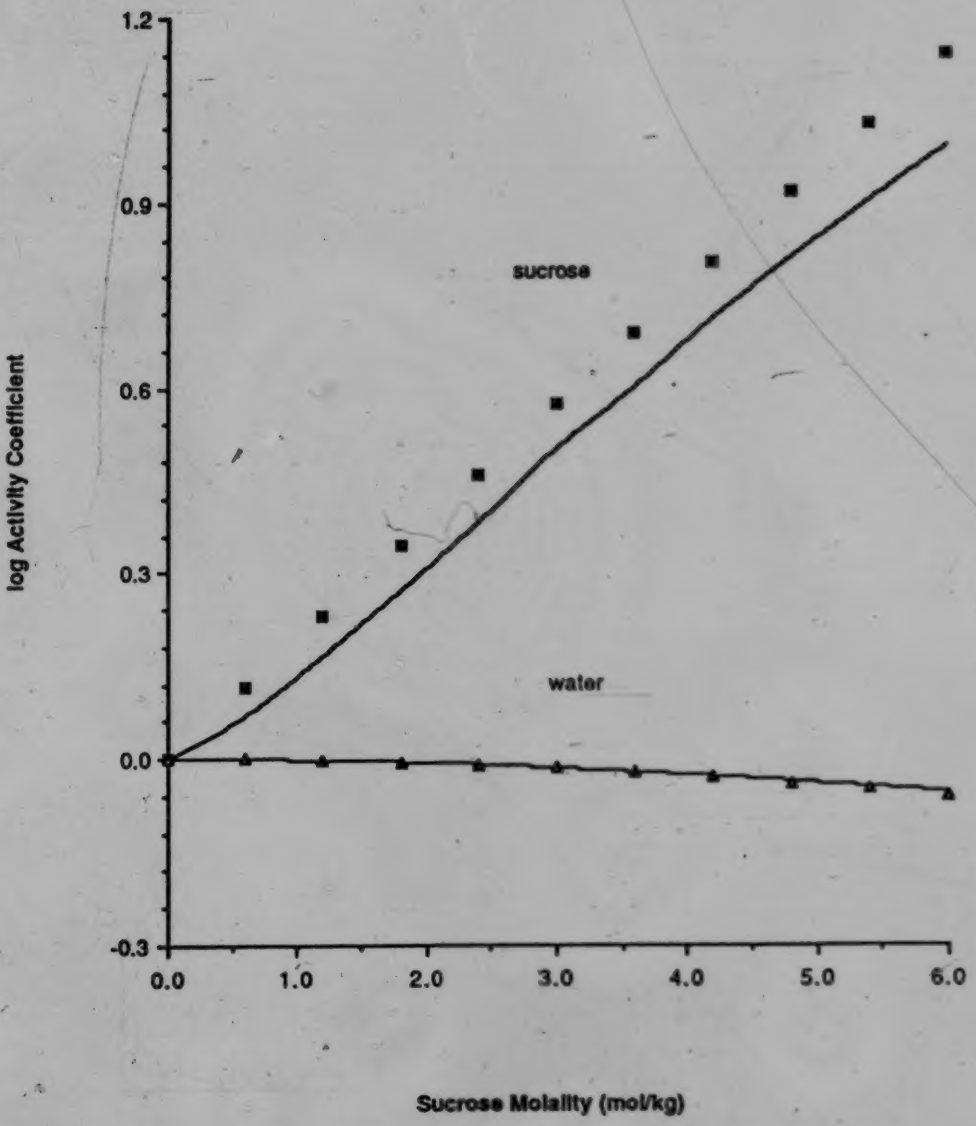

Figure 4.8 Predicted (-) and experimental sucrose (■) and water (Δ) activity coefficients at 55.7°C. Experimental data adapted from Honig (1953).

the solution freezing point depression, boiling point elevation and sucrose solubility. See sections 5.3.2, 5.3.3 and 5.3.4.

4.6 Ternary Solutions

The three aqueous binary systems in the representative food solution have been correlated with the extended UNIQUAC equation. The required parameters were taken from the literature or estimated from experimental data. Experimental activity coefficient data for the remaining non-aqueous binary systems, ethanol-sodium chloride, ethanol-sucrose, and sucrose-sodium chloride, are not available in the literature, consequently, the remaining parameters must be estimated based on experimental data on the aqueous ternary solutions.

4.6.1 Aqueous sodium chloride-ethanol solutions

The thermodynamic behavior of aqueous solutions of ethanol and sodium chloride has been studied by a number of researchers. Smirnov and his colleagues (1980, 1981) measured the liquid phase, rational mean activity coefficient of the salt in solutions with solvent concentrations varying from 0 to 70 mol % ethanol at 25°C using solution conductivities. Furter (1958) and Mondeja-Gonzalez (1973) measured the vapour-liquid equilibria of saturated solutions of salt, ethanol and water under atmospheric pressure. Expressions for the component activity coefficients were developed based on these data and used to estimate the required parameters. These expressions and their development are given in Appendix 4.

It is assumed in the extended UNIQUAC equation that the electrolytes present are strong electrolytes. In the aqueous system, sodium chloride is almost completely ionized over the its entire concentration range (Skoog and West, 1963). The ready solubility of so many electrolytes in water is due primarily to the high dielectric constant of the solvent which in turn is due to the polar nature of the water molecule and its favouring of a tetrahedrally coordinated structure (Robinson and Stokes, 1959). With a decrease in the dielectric constant, the strength of the electrostatic interactions between ions of opposite charge is increased and the probability of ion pair formation is also increased. The extent of ion association or ion pair formation may be determined using conductivity measurements (Harned and Cook, 1939). These interactions may have a significant effect on the behavior of the solution and must be considered in the study of salt/mixed solvent systems

Spivey and Shedlovsky (1967) studied the conductance of solutions of sodium chloride in aqueous ethanol. They found no evidence of significant ion pair formation in solutions of up to 80% ethanol by weight, or 53 mol % ethanol on a binary basis. At this concentration, the dielectric constant of the solvent is 32.8 (Sen *et al.*, 1979). To ensure that the effect of ion pair formation in solutions of high ethanol concentration is not a factor, the parameter estimation was based on experimental data for systems of solvent concentrations of 50 mol % (salt-free) or less.

The bulk dielectric constant and density of the solvent mixture is required in the calculation of the Debye-Hückel limiting law. These properties are correlated from experimental data. (See Appendix 3.)

The application of the extended UNIQUAC equation to the sodium chloride-ethanol-water system requires the estimation of three additional parameters: the UNIQUAC ion-ethanol interaction parameters (U_{ij}) and the Brønsted-Guggenheim, solvent parameter for aqueous ethanol (B_{EtOH}).

The contributions from the three terms in the equation to the individual component activity coefficients were assessed to determine the relative importance of each term. These contributions are shown in Figures 4.9-4.11 in a ternary solution with a constant solvent composition of 10 mol % ethanol.

As Figure 4.9 illustrates, in the low salt concentration range, the rational mean salt activity coefficient is dominated by the Debye-Hückel limiting law, and is therefore a function only of the physical properties of the solution. The UNIQUAC and Brønsted-Guggenheim terms are not significant in this range. At higher salt concentrations, these terms have more influence. The UNIQUAC interaction parameters and Brønsted-Guggenheim solvent parameter (B_{EtOH}) required for this system, should therefore

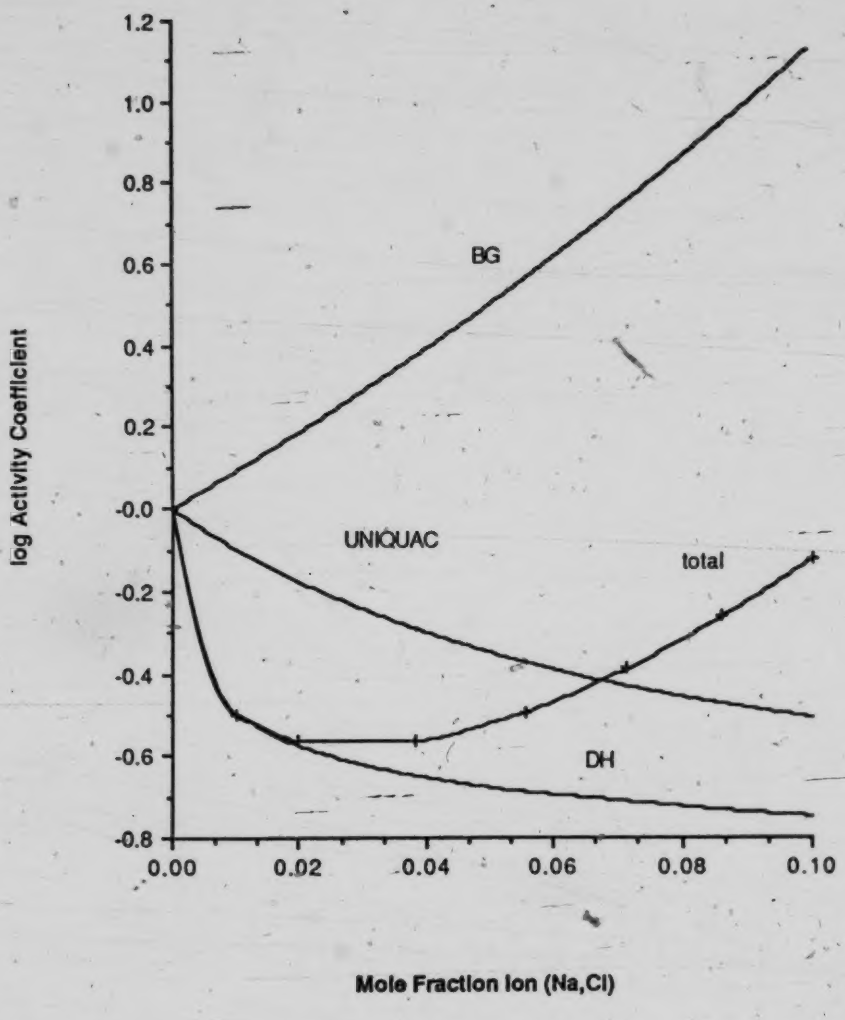

Figure 4.9 Contributions to the salt activity coefficient (+) in ethanol-salt-water systems calculated with equation 3.3.20 : solvent composition 10 mol % ethanol (salt-free).

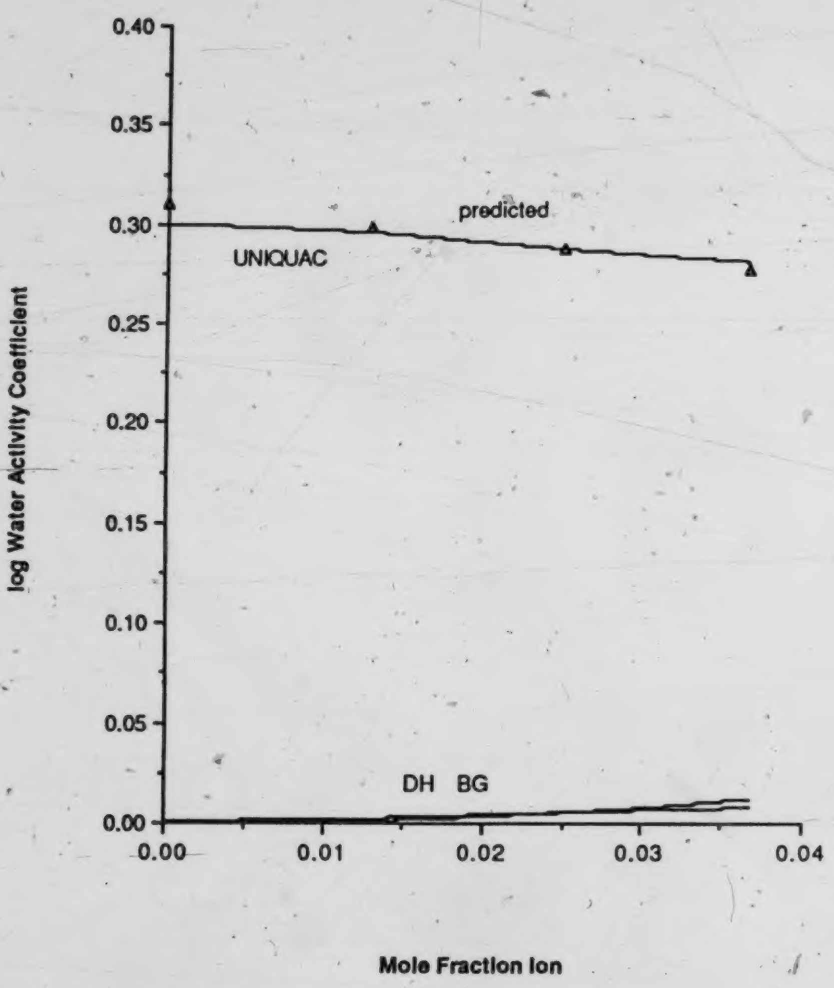

Figure 4.10 Contributions to the water activity coefficient (Δ) in ethanol-salt-water systems calculated with equation 3.3.19 : solvent composition 10 mol % ethanol (salt-free).

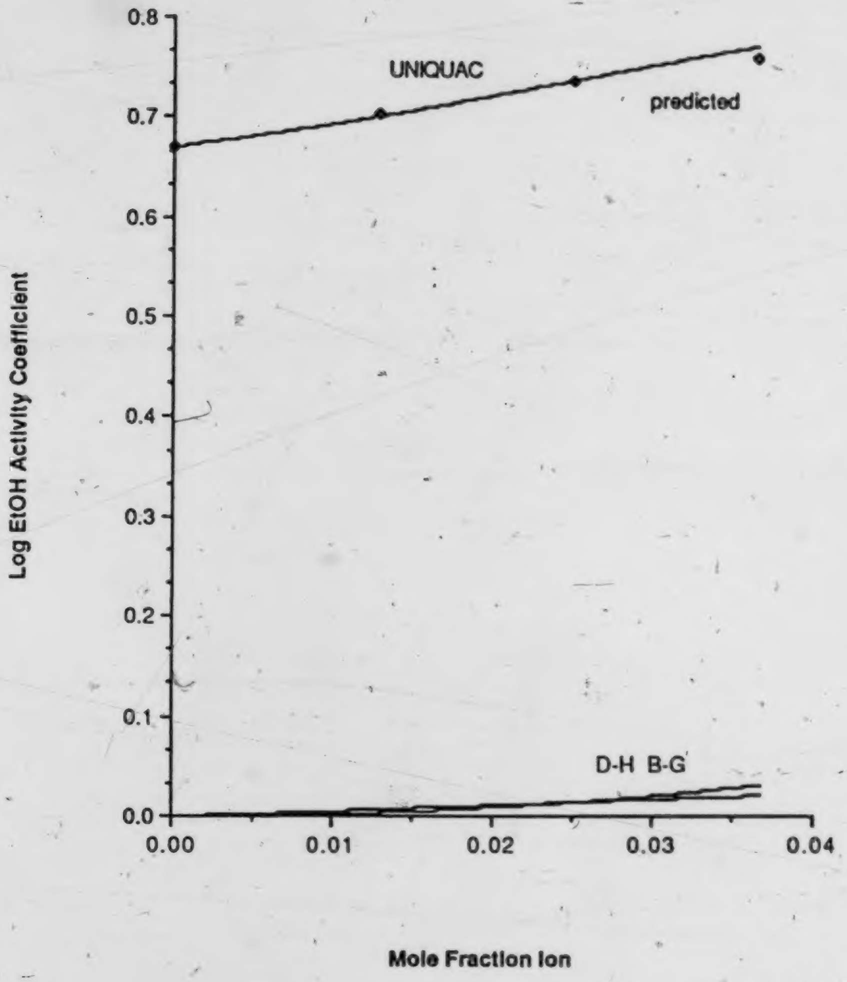

Figure 4.11 Contributions to the ethanol activity coefficient (♦)in ethanol-salt-water systems calculated with equation 3.3.19 : solvent composition 10 mol % ethanol (salt-free).

be estimated based on experimental salt activity coefficients upon which they have a significant influence. To do this, a weighting procedure was used. Experimental salt activity coefficients in the dilute concentration range in which the contribution of the Debye-Hückel limiting to the calculated activity coefficient was 85% or more were given a weight of 1. The remaining data were weighted with a factor of 10.

Figures 4.10 and 4.11 illustrate the contributions to the calculated water and ethanol activity coefficients. These quantities are determined primarily from the UNIQUAC term, with minor contributions from the remaining terms only at high salt concentrations. The required parameters should be estimated based on experimental solvent activity coefficients, over the entire concentration range.

The over-all optimization procedure was performed using data from two different sources, vapour-liquid equilibria and conductivity measurements. The data from these two sources differed both in the precision of the measurements and the number of experimental points available.

To account for the number of data points used from each source, the total Chi-square (χ^2) was divided into two parts; one based on the salt activity coefficients and the second from the solvent activity coefficients. The total Chi-square used in the overall optimization of the required parameters was calculated as follows:

$$\chi^2_{total} = w_{salt}\chi^2_{salt} + w_{solvents}\,\chi^2_{solvents} \qquad [4.6.1]$$

Where the weighting factors w_{salt} and $w_{solvents}$ are inversely proportional to the number of data points from each source used and χ^2_{salt} and $\chi^2_{solvents}$ are the Chi-square statistics based on the salt and solvent activity coefficients respectively. The Chi-square values were calculated using equation 3.5.2. The weighting parameters (w_i) are uniform for the solvent activity coefficients and have values of 1 or 10 for the salt activity coefficients as discussed previously.

A maximum value of 5000 K is placed on the UNIQUAC interaction parameters (U_{ij}). This value is equal to the energy of interaction between ions of like sign, indicating the exclusion of this interaction from the determination of the short-range interactions. Therefore, a constrained optimization (Toupin, 1986) of the UNIQUAC parameters was performed. The optimal values of the ion-ethanol interaction parameters were found, from the constrained search, to be 5000 K. When the constrant was removed., these parameters were found to increase to larger values indicating neglible interaction between these two components. These parameters were set to 5000 K, the maximum value of the parameter in the model and the system fitted based on a single parameter, B_{EtOH} (Table 4.3).

The rational, mean salt activity coefficients predicted using the extended UNIQUAC equation and generated from polynomials based on the experimental data of Smirnov *et al.* (1980,1981); (See Appendix 4), in solutions of constant solvent compostions: 10, 30 and 50 mol % ethanol (salt-free) are presented in Figures 4.12 - 4.14. The average %RMSD of the salt activity coefficients in these solutions were 5%, 7.5% and 8.9% respectively with the maximum error occuring in the dilute solutions. This error does not exceed 25%. The predicted and experimental solvent activity coefficients in aqueous ethanol solutions saturated with salt at atmospheric pressure are presented in Figure 4.15. The experimental values are calculated from the data of Furter(1958) and Mondeja-Gonzalez (1974). (See Table 11.3 and Appendix 4).

Considering the concentration range covered, the results are of acceptable accuracy. The % root-mean squared deviation (%RMSD) between the predicted and experimental activity coefficients is approximately 10%. The relatively large deviations in the activity coefficients are due mainly to deficiencies in the model, particularly in the low salt concentration range, where the salt activity coefficient is dominated by the Debye-Hückel limiting law.

Mock and his coworkers (1986), in their application of an electrolyte-NRTL model to systems of electrolytes in mixed solvents found an expression that correctly represents the long-range ion-ion interactions in the excess Gibbs energy of these systems lacking. The Pitzer-Debye-Hückel expression, adapted successfully by Chen and Evans (1986) as the long-range interaction contribution in aqueous

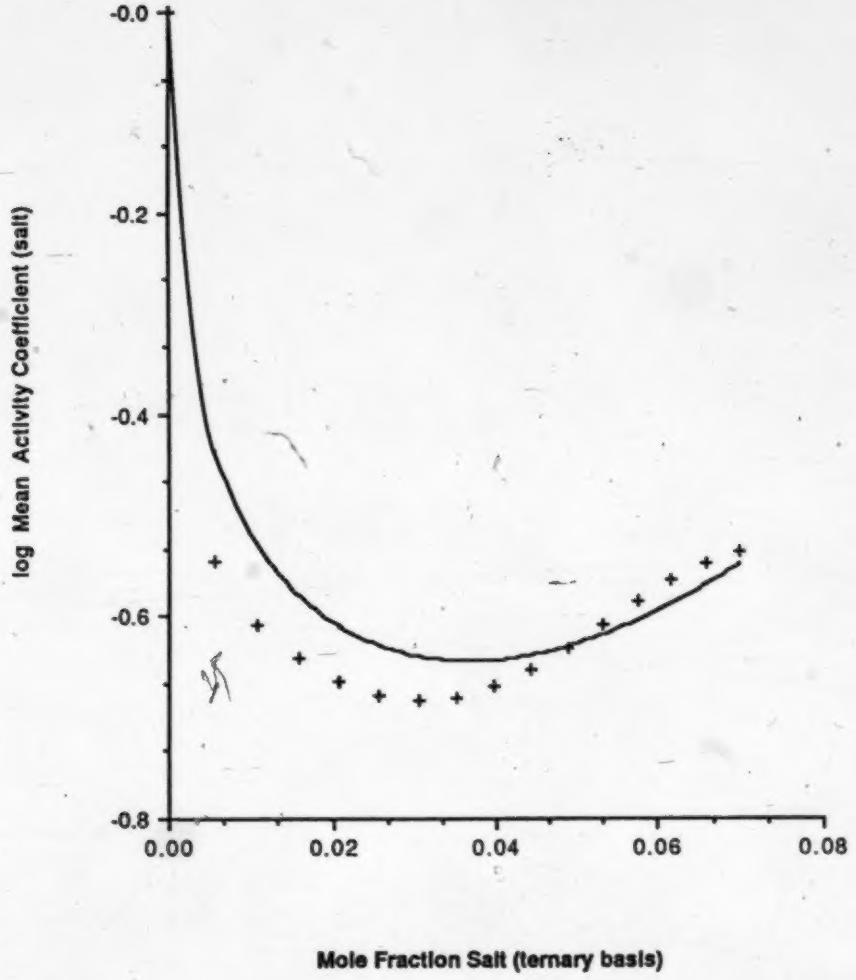

Figure 4.12 Predicted (-) and experimental salt activity coefficient (+) at 25°C.: 10 mol % ethanol (salt-free). Expt data adapted from Smirnov *et al*. (1980, 1981).

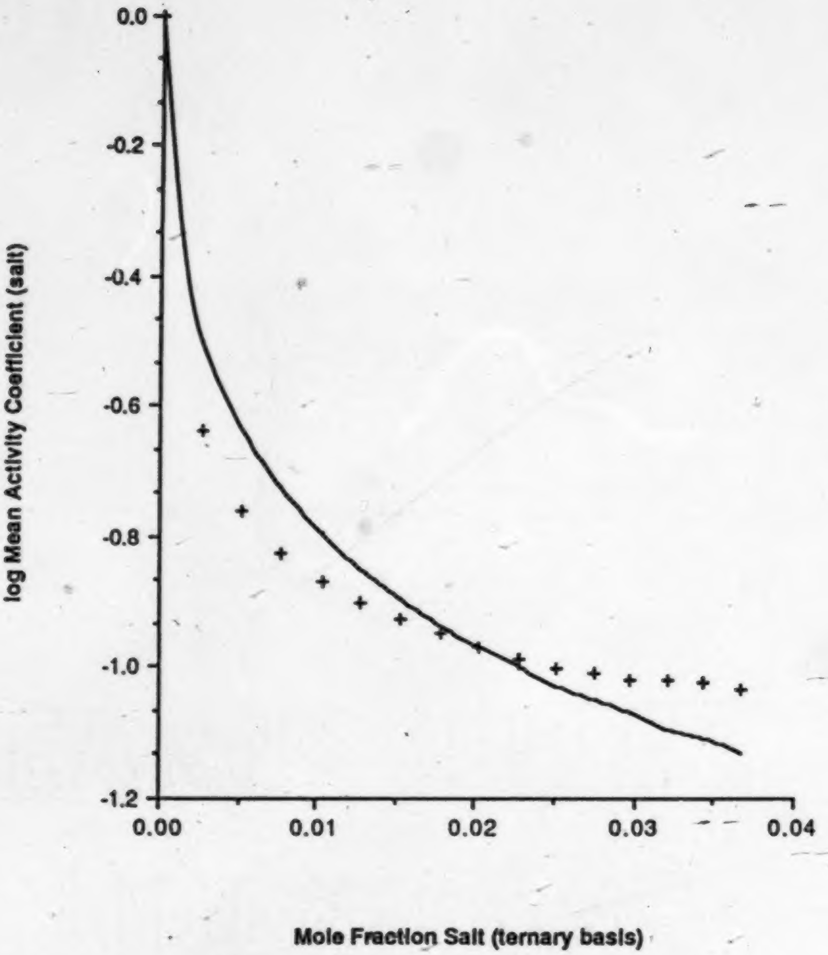

Figure 4.13 Predicted (-) and experimental salt activity coefficient (+) in aqueous ethanol at 25°C. : 30 mol % ethanol (salt-free). Expt. data adapted from Smirnov *et al.* (1980, 1981).

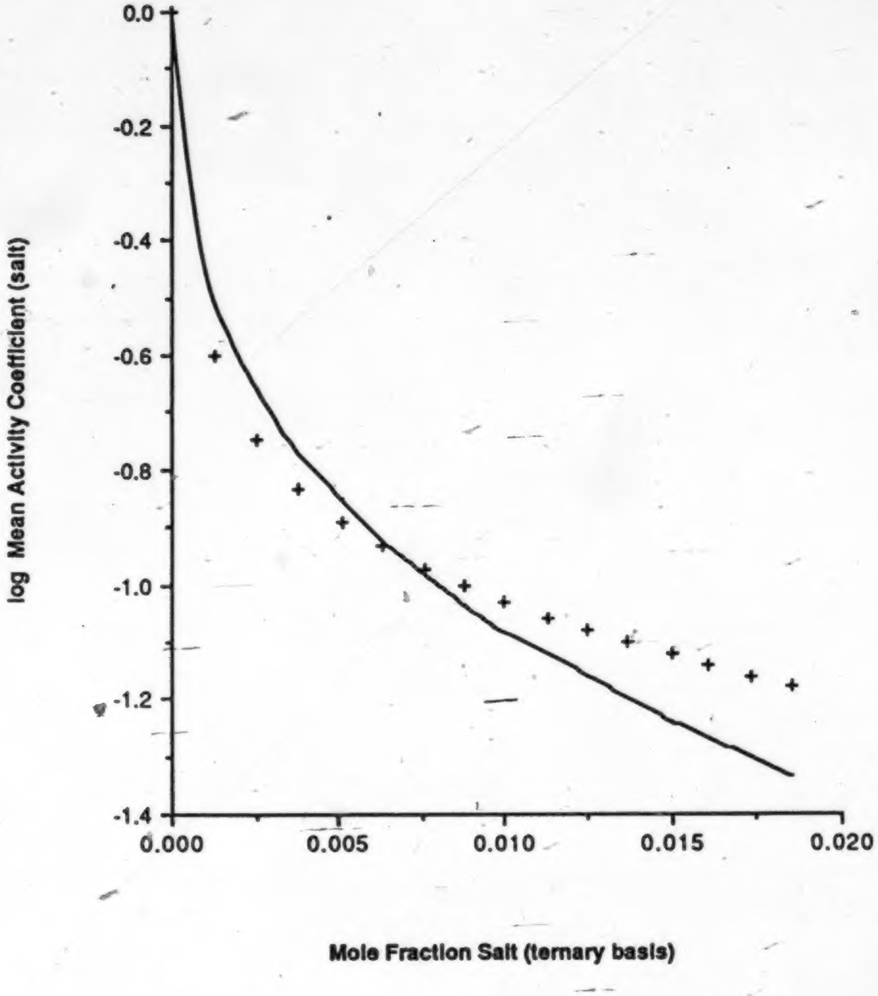

Figure 4.14 Predicted (-) and experimental salt activity coefficient (+) in aqueous ethanol at 25°C. : 50 mol % ethanol (salt-free). Expt data adapted from Smirnov *et al.* (1980, 1981).

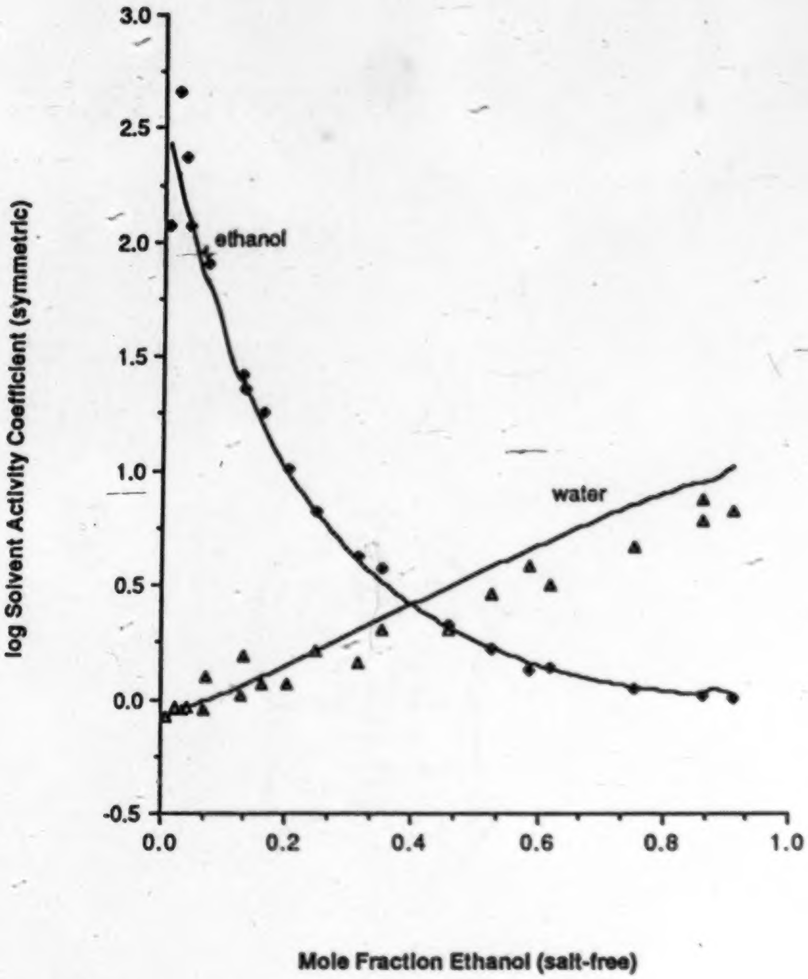

Figure 4.15 Predicted (-) and experimental ethanol (♦) and water (Δ) activity coefficients in saturated solutions at 760 mm Hg. Expt. data from Furter (1958) and Mondeja-Gonzalez (1973)

solutions, was not adequate for mixed solvent systems. This expression fails to take into account the influence of changes in density and dielectric constant in the mixed solvent system on these interactions. Mock *et al*. found the influence of the interionic interactions on the solvent activity coefficients to be neglible and neglected these interactions in the calculation of the equilibrium vapour compositions of electrolyte/mixed solvent systems.

The extended UNIQUAC equation presented by Sander and his coworkers (1986a), for the calculation of vapour-liquid equilibria of mixed solvent/electrolyte systems does not contain the empirical Brønsted-Guggenheim term. These reseachers also found the Debye-Hückel limiting law inadequate. To improve the representation Sander introduced an empirical correction to the Debye-Hückel parameter (A).

The predicted solvent activity coefficients are validated with the prediction of the salting-out effect on the vapour-liquid equilibria of this system. See section 5.3.5.

4.6.2 Aqueous sucrose-sodium chloride solutions

Robinson and his colleagues (1970) studied the thermodynamic behavior of ternary solutions of sodium chloride, sucrose and water at 25° using an isopiestic vapour pressure method. The solute concentrations varied from 0 to 6 molal on an aqueous molality basis in each solute. The authors present expressions for the activity coeffients of each solute as functions of the two solute concentrations. (See Appendix 4.)

The physical properties of the aqueous sucrose solutions required for the Debye-Hückel limiting law are estimated from the previously mentioned correlations. (See Appendix 3.)

The extent of ion association in this system has not been well determined although some work has been done on dilute solutions. Mohanty and Das (1982) and Stokes and Stokes (1956) studied the conductance of sodium chloride in aqueous sucrose solutions to determine the extent of ion association. Both report complete ionization of the salt in solutions of up to 20 % sucrose (weight-basis). These studies however, are limited to dilute salt concentrations. Stokes and Stokes (1956) conclude that the ions maintain much the same state of solvation in the solution as in water.

In aqueous solutions of 6 molal sucrose, the sucrose molecules are greatly outnumbered by water molecules, the two being present in a ratio of 1:9. The solvent in these solutions remains largely water. In addition to this, the dielectric constant of this solution is fairly high, a 6 molal solution has a dielectric constant of aproximately 55. Based on these observations, it was assumed that the extent of ion association, over the entire concentration range was neglible, the salt remaining essentially as independent ions at all concentrations considered. This assumption requires experimental confirmation.

The estimation of three parameters was required for the application of the extended UNIQUAC equation to this system, two UNIQUAC interaction parameters representing the ion-sucrose molecule interactions and the Brønsted-Guggenheim solvent parameter for sucrose solutions (B_{suc}).

The parameter estimation was performed based on experimental salt and sucrose activity coefficients generated from the expressions presented by Robinson *et al.* (1970) and adjusted as shown in Appendix 4. The weighting procedure used in the sodium chloride-ethanol-water system for the dilute salt activity coefficients was also used for this system. No weighting of data sets was required.

The solute activity coefficients predicted using the extended UNIQUAC equation and adapted from the expressions of Robinson and Stokes (1974) at 25°C are shown in Figures 4.16-4.18 at sucrose concentrations of 1, 3, and 5 molal (salt-free). The parameters used for this system are shown in Tables 4.1, 4.2 and 4.3.

Considering the concentration range of both solutes, the equation does an acceptable job representing solute activity coefficients of the system. The average %RMSD of the salt activity coefficient ($\gamma_{\pm}^{*}$) over the entire concentration range is 8%. The sucrose activity coefficient is predicted with an average %RMSD of 5%. The validity of the solute activity coefficients is tested with the prediction of the solute solubilities in ternary solutions

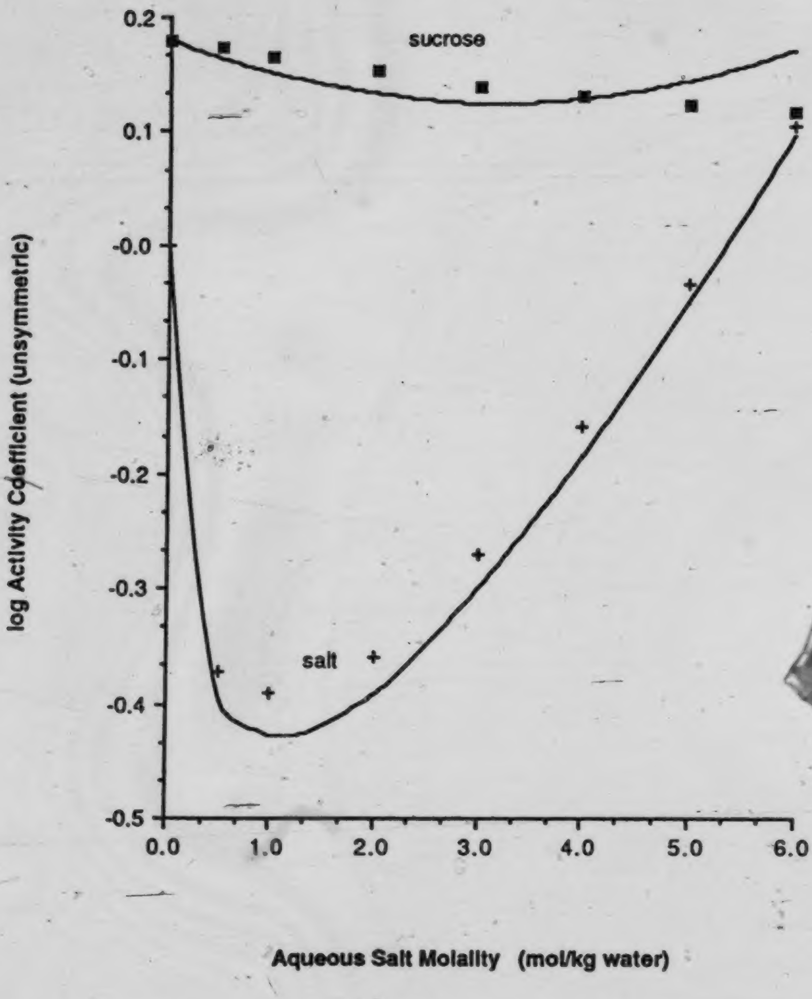

Figure 4.16 Predicted (-) and experimental sucrose (■) and salt (+) activity coefficients at 25°C. Sucrose concentration: 1 mol/kg water. Experimental data adapted from Robinson *et al.* (1970).

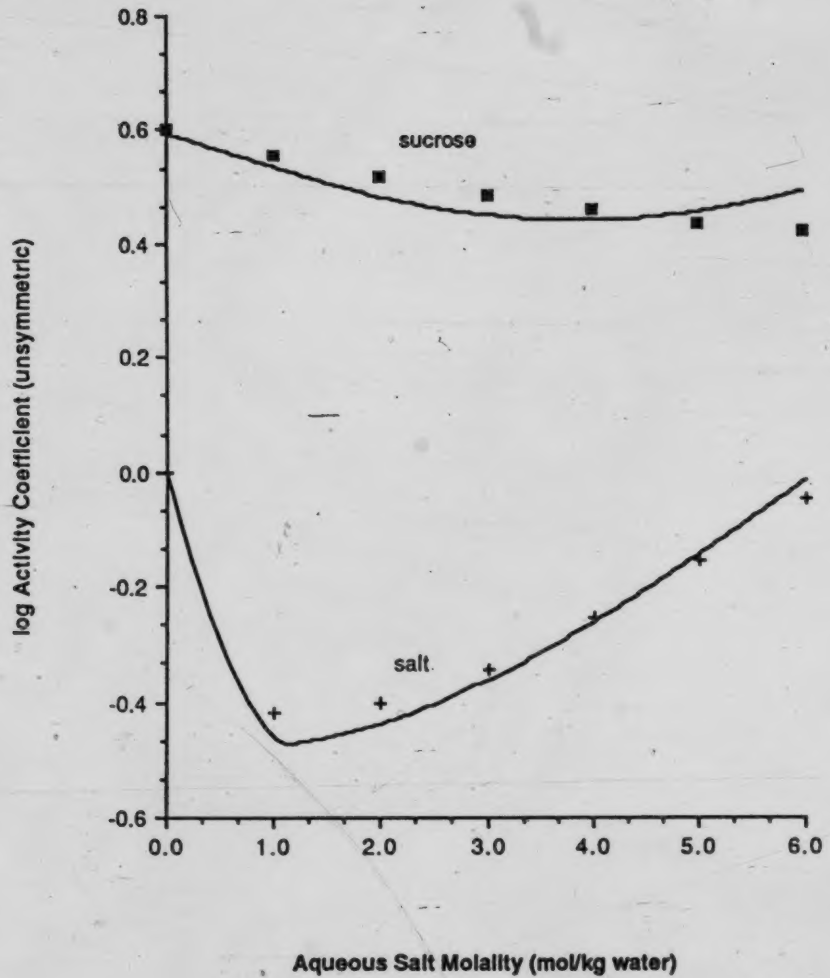

Figure 4.17 Predicted (-) and experimental sucrose (▪) and salt (+) activity coefficients at 25°C. Sucrose concentration: 3 mol/kg water. Experimental data adapted from Robinson *et al.* (1970).

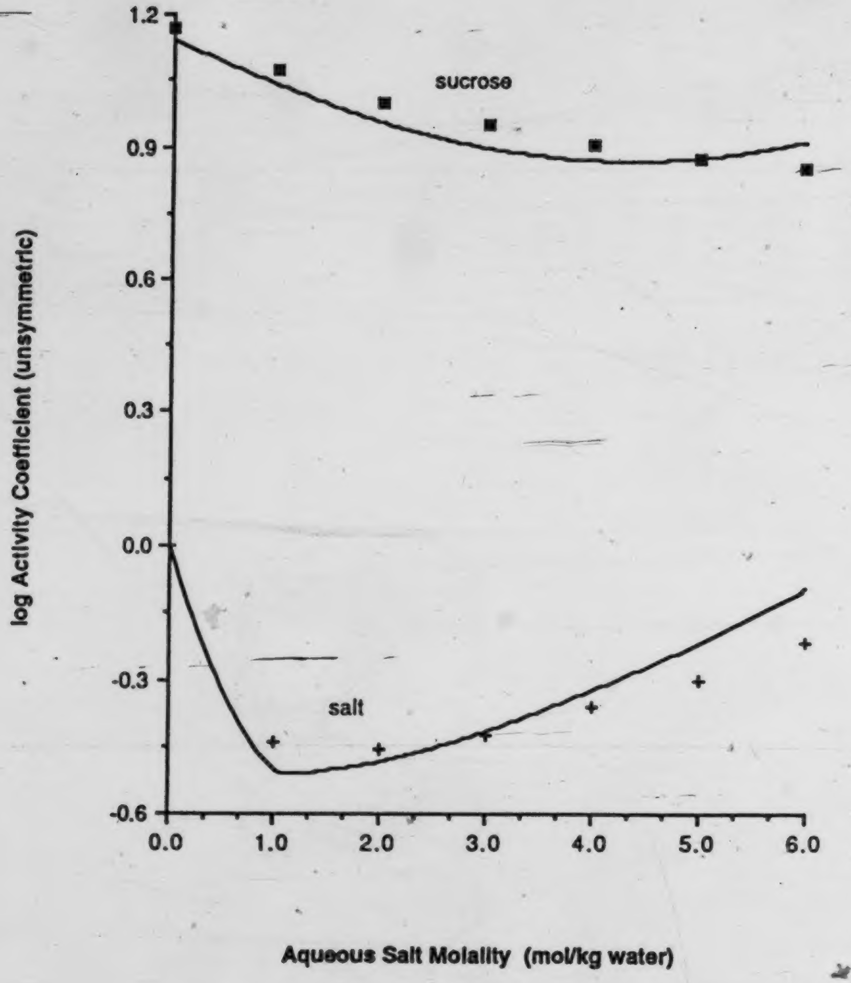

Figure 4.18 Predicted (-) and experimental sucrose (■) and salt (+) activity coefficients at 25°C. Sucrose concentration: 5 mol/kg water. Experimental data adapted from Robinson *et al.* (1970).

of sucrose, salt and water. See section 5.3.4.

4.6.3 Aqueous ethanol-sucrose solutions

Experimental data for aqueous ethanol sucrose system are available in the literature as sucrose solubilities in mixtures of aqueous ethanol. Data of this type have been published by Haeseler and his colleagues (1968) at 20°C and by West (1933) at 14°C. Based on these data, estimates of the unsymmetric sucrose activity coefficient at saturation may be made. (See Appendix 4). Estimates of the precision of the experimental data are not available. It was therefore assumed that the relative error on the activity coefficients was uniform for the entire data set and each data point was weighted equally.

This system is entirely represented by the UNIQUAC equation and requires the estimation of a single UNIQUAC interaction parameter (U_{ij}) representing the interaction between sucrose and ethanol. The optimized value of this parameter is presented in Table 4.1. The predicted and experimental (Table 11.4) sucrose activity coefficients in saturated solutions are shown in Figures 4.19 and 4.20. The %RMSD of the predicted and experimental activity coefficient is 37%. Considering that a single parameter was estimated and the system is highly non-ideal containing dilute solutions in which the precision of the data is questionable, the accuracy is acceptable. In addition to this only data from solutions saturated with sucrose was

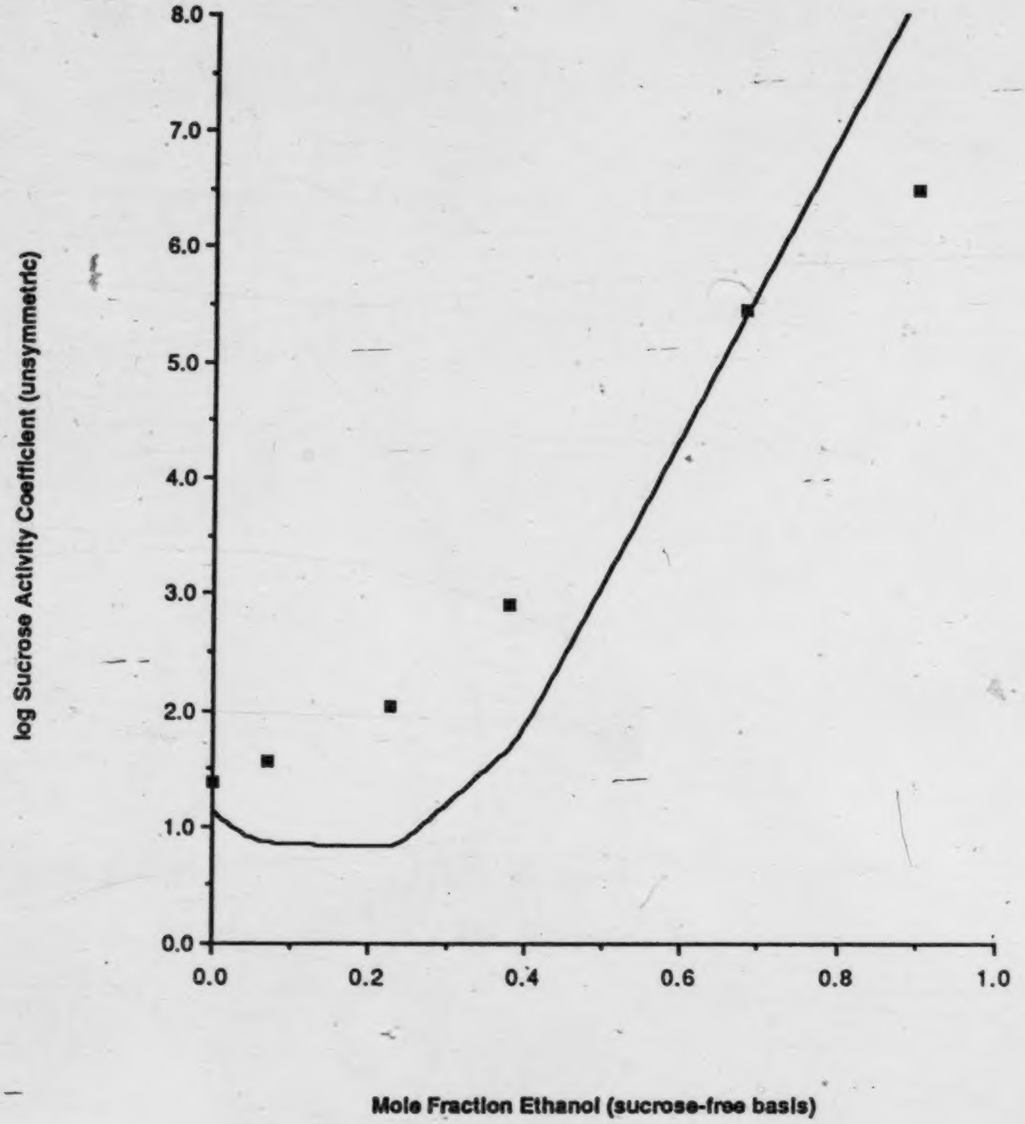

Figure 4.19 Predicted (-) and experimental sucrose (■) activity coefficient in aqueous ethanol solutions saturated with sucrose at 14°C. Expt. data from West (1933).

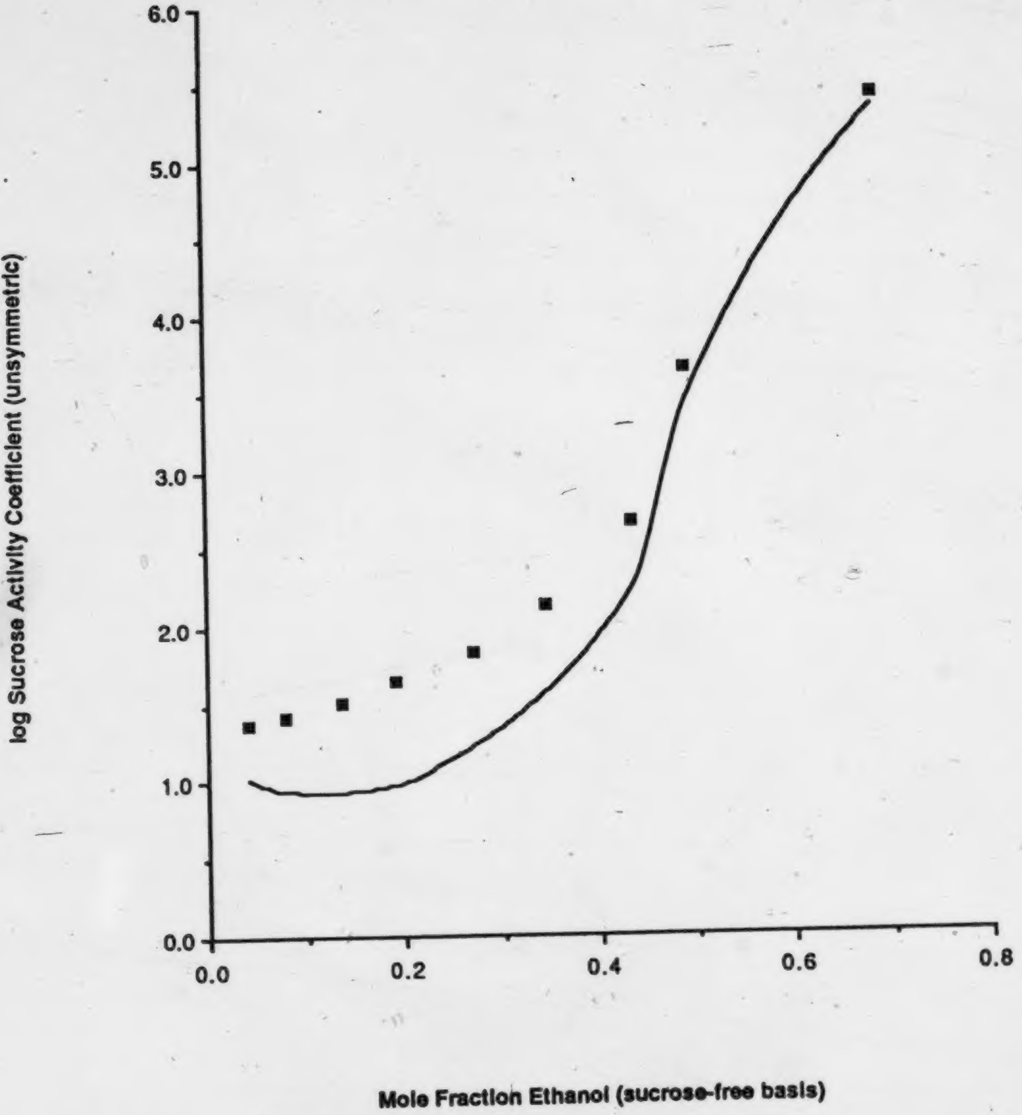

Figure 4.20 Predicted (-) and experimental sucrose (▪) activity coefficient in aqueous ethanol solutions saturated with sucrose at 20°C. Expt. data from Haeseler *et al.* (1968).

used. At this concentration it is not clear whether the solid was precipitated as a pure crystal (See Section 5.3.4).

4.7 SUMMARY

The parameters required for the application of the extended UNIQUAC equation to the model food solution are summarized, with their estimated errors, in Tables 4.1 and 4.3. The volume (r_k) and surface area parameters (q_k) for this system, required are presented in Table 4.2. Considering the complexity of the system involved, the accuracy of the predicted activity coefficients in the system is good. The utility of the model in food engineering applications, notably in the design and simulation of food process is clear, particularly in light of the state of thermodynamic modelling in the food industry alluded to earlier. The model, however, has significant limitations. These result from the limited thermodynamic data available on food systems and the assumptions inherent in the model which cannot be applied to these systems.

4.7.1 Quality of experimental data

Only a limited amount of experimental data on systems important in food engineering applications are available in the literature. The data available, are often incomplete and of questionable accuracy. In their study of the vapour-liquid equilibria of mixed solvent/salt systems, Sander and

Table 4.1 UNIQUAC interaction parameters (U_{ij})(K)

Component	Water	Ethanol	Sucrose	Na^+	Cl^-
Water	0.0	380.68[a]	55±2	-693.1[b]	1240.1[b]
Ethanol	-64.56[a]	0.0[a]	134±4	5000	5000
Sucrose	55±2	134±4	-37.4±.8	2734±8	1139.7±.6
Na^+	-693.1[b]	5000	2734±8	5000[b]	0.0[b]
Cl^-	1240.1[b]	5000	1139.7±6	0.0[b]	5000[b]

[a] from Prausnitz *et al.* (1980)
[b] from Christensen *et al.* (1983)

Table 4.2 UNIQUAC volume (r_k) and surface area (q_k) parameters

Component	r_k	q_k
Water	0.92[a]	1.40[a]
Ethanol	1.211[a]	1.97[a]
Sucrose	9.1±.1	8.5±.1
Na^+	.1426[b]	.2732[b]
Cl^-	.9861[b]	.9917[b]

[a] from Prausnitz *et al*. (1980)
[b] from Christensen *et al*. (1983)

Table 4.3 Brønsted-Guggenheim solvent parameters $B_{solvent}$(K)

Solvent	$B_{solvent}$	Standard estimate of error
Aqueous ethanol	77	4
Aqueous sucrose	17.2	0.3

β_o water = 60.9 (Christensen *et al.*, 1983) his coworkers (1986a) had similar difficulties with data obtained from the literature. The data were found to be incomplete and scattered, with significant inconsistencies between reported data sets.

The data available on food systems such as aqueous sucrose are reported over limited temperature and concentration ranges. These data are not of sufficient precision to confidently determine the temperature dependency of the model parameters. This temperature dependency is required for a consistent representation of vapour-liquid, liquid-liquid and heats of mixing from a given model (Renon, 1985). The parameters optimized in this study have been optimized over a limited temperature range and care should be taken in their application to systems under conditions outside this range.

4.7.2 Ionic interactions

The predominance of the electrostatic contribution to the salt activity coefficient, illustrated in section 4.6.1, is due primarily to the strength of the ionic interaction which is considerably larger than the strength of non-ionic forces. The electrostatic interactions are particularly significant in dilute salt solutions due to the inverse-square relationship between these interactions and the interionic distance. Electrostatic forces have a much longer range than other intermolecular forces which depend on higher powers of the reciprocal distance (Prausnitz *et al.*, 1986).

The inability of the extended UNIQUAC equation to represent the dilute salt activity coefficient in mixed solvents, may be attributed to the failure of the Debye-Hückel limiting law to properly represent the interionic forces in mixed solvents. The variation in the solution dielectric constant with ion concentration is not accounted for. In the Debye-Hückel limiting law, the bulk dielectric constant of the pure solvent is used. This quantity is valid only in the limit of infinitely dilute solutions (Debye and Pauling, 1925). The electric field around small ions is strong enough to orient the surrounding water molecules resulting in local dielectric saturation. At higher ion concentrations this results in a noticable reduction of the macroscopic dielectric constant of the solution (Ball *et al.*, 1985a). In the Debye-Hückel limiting law, the logarithm of the ionic activity coefficient is inversely proportional to the dielectric constant (See equation 3.3.6). As Figure 4.9 illustrates, the Debye-Hückel limiting law under-predicts this value when the bulk solvent dielectric constant is used. If it is assumed that the mixed solvent behaves in a way similar to water (i.e. the solution dielectric constant decreases with increased ion concentration), the inability to properly reflect the behavior of the salt activity coefficient is due to the inaccuracy of the dielectric constant used in the expression.

Cruz and Renon (1978) take this effect into account with an empirical expression to calculate the variation of the solution dielectric constant with ion concentration, while Ball *et al.* (1985a) cite the work of Pottel in their expression for this quantity.

An analogous expression to Pottel's for mixed solvents does not exist. An improved representation of the experimental data is possible with an empirical fitting of the Debye-Hückel parameter (A) (Sander *et al.*, 1986a), however, in a model designed for engineering purposes, the use of the bulk dielectric constant of the solvent was preferable to the inclusion of additional parameters.

4.7.3 The UNIQUAC equation

The inability of the extended UNIQUAC equation to correctly represent the partial molar entropy of some solutions using the van der Waals geometric parameters is illustrated in the aqueous sucrose system (Section 4.5.3). These parameters were fitted empirically with estimates of the component entropies based on experimental data, indicating that the geometric properties of the sucrose molecule in solution are not represented well by values estimated based on the molecular crystal. The term used to represent the excess entropy however may also be in error (Kikic *et al.*, 1980; Alessi *et al.*, 1982).

The combinatorial term in the UNIQUAC equation is based on the Guggenheim-Staverman equation. Sayegh and Vera (1980) discuss the limitations of this term and find the expression leads to poor results if mixtures of bulky molecules are considered. The bulkiness of a molecule is reflected by the value of l_k (see equation 3.3.4.) This value is assumed to be the same in solution as it is in the pure state, which may also lead to errors in the representation of the solution excess entropy (Sayegh and Vera, 1980).

Similar problems may be encountered in the representation of the ions in solution. The Pauling ionic radii, based on the crystal state, are used to calculate the volume and surface area parameters of the ion (Christensen *et al.*, 1983). Marcus (1983) has studied the radii of different ions in aqueous solution using x-ray and neutron diffraction techniques. He presents a list of aqueous ionic radii for 35 ions. These values were found to be close to the Pauling radii which were recommended for use in aqueous solution, if the aqueous ionic radii were not available. Marcus' study, however, was limited to aqueous solutions with the reported ionic radii were based on the average distance between the centre of the ions and the centre of the nearest water molecule. In mixed solvents, these distances may differ significantly.

In the UNIQUAC equation, the interaction between any two species in solution are assumed to be uniform throughout the solution. The estimation of a single parameter to represent the average interaction of ion-water interactions at all concentrations does not allow for the fact that the type and number of interactions will vary with the solution concentration. It has been reported that the size of the hydration shell changes with ion concentration (Maurer, 1983).

Skjøld-Jorgenson *et al.* (1982) treat this problem by introducing concentration dependent interaction parameters (U_{ij}). Sander *et al.* (1986a) also include this concentration dependency in their extended UNIQUAC equation.

Perhaps the most significant assumption in the UNIQUAC equation limiting its application is the non-randomness assumption. The non-randomness of a solution is related to the net energy of interaction through the Boltzman constant (Wilson, 1964). It has been suggested that this assumption is too strong and over-corrects for deviations from random mixing (Hu *et al.*, 1983; Prausnitz *et al.*, 1986).

The many modifications made to the UNIQUAC equation, although empirical in nature, have resulted in improved representation of specific systems. The UNIQUAC equation should however, be considered a semi-empirical equation (Renon, 1985) requiring parameters estimated from experimental data. The parameters have physical meaning because the equation is theoretically based, but often many different effects are combined in a single parameter.

4.7.4 Significance of parameters

Three types of parameters have been estimated in this study: the Brønsted-Guggenheim solvent parameter for aqueous ethanol and aqueous sucrose solvents, geometric parameters q_k and r_k of the sucrose molecule in solution, and a number of UNIQUAC interaction parameters (U_{ij}). The Brønsted-Guggenheim parameter is an empirical parameter representing the interaction between ions of opposite charge. Its empirical nature makes it difficult to attach any physical meaning to it. It may be stated generally, based on equation 3.3.9, that an increase in the value of β indicates increased interaction between the ions and a resulting increase in the excess Gibbs energy of the solution.

The significance of the volume (r_k) and surface area (q_k) parameters is straightforward, noting, however, that these parameters represent molecules in solution. The surface area parameter, in particular, may be affected by the configuration of the molecule in this state compared to its crystal state.

The UNIQUAC interaction parameter (U_{ij}) represents the potential energy of two nearest neighbours in a mixture of components i and j, component j being the central ion (Abrams and Prausnitz, 1975). The net interaction energy (a_{ij}), is a more appropriate parameter to interpret from a physical standpoint. The net interaction parameter calculated as

$$a_{ij} = U_{ij} - U_{jj} \qquad [4.8.1]$$

represents the net energy of interaction between molecules i and j compared to the energy of interaction between two molecules of component j.

The net interaction parameter is also used to calculate the local composition around a central molecule. A positive value of a_{ij} indicates a net repulsive interaction and results in a lower local concentration. A value of zero indicates no net interaction and results in random mixing, with the local composition equivalent to the stoichiometric composition, such a solution has zero enthalpy of mixing. A negative value of a_{ij} indicates negative deviation from ideality (Wilson, 1964).

Caution should be observed when attempting to correlate the net interaction parameters of the ions in the extended UNIQUAC with their behavior in solution. The dominant forces governing the behavior of ions in solution are the interionic, electrostatic interactions. These forces are accounted for in the equation with the Debye-Hückel limiting law and, consequently, the ions must be thought of as neutral species when considering the short-range, non-ionic forces. The local composition, however, is strongly influenced by the ionic interactions.

5. APPLICATIONS OF THE EXTENDED UNIQUAC EQUATION

The extended UNIQUAC equation provides a reasonable estimation of the component activity coefficients in the aqueous binary and ternary sub systems of the representative food system under normal conditions of temperature and pressure, particularly in light of the lack of experimental data on these systems. The equation was applied in a number of different situations to demonstrate its usefulness. To illustrate the utility of the model for systems for which data do not exist, activity coefficients in the quaternary sodium chloride-sucrose-ethanol-water system were predicted. Terpenes are important aroma compounds in some food systems. The model has been applied to predict the behavior of aqueous solutions of sucrose or sodium chloride saturated with three terpenes.

Accurate phase equilibrium descriptions are necessary for any acceptable design or simulation of separation processes (Urlic *et al.*, 1985). The extended UNIQUAC was employed to predict a number of physical properties, based on phase equilibria, in the model food system. These results will be discussed. The chapter concludes with a discussion of the application of the equation to the modeling of mass transfer in biological systems.

5.1 Quaternary Solutions

No experimental data for quaternary sucrose-sodium chloride-ethanol-water system are available in the literature. The application of the extended UNIQUAC equation to this system therefore, involved only the prediction of the component activity coefficients with no method for the validation of these results. Experimental measurements of the density and dielectric constant of the ternary solvent are not available. These properties were calculated from the density and dielectric constants of the aqueous binary solutions using an appropriate mixing rule. (See Appendix 3). Bondi (1968) suggests that an estimate of the specific volume of a multicomponent solution may be made with the weighted average of the components in the mixture. There is no theory for the prediction of the excess volume of mixing (Bondi, 1968) and consequently this quantity is neglected. The following expression is used to calculated the density of the multicomponent solvent mixture:

$$\frac{1}{\rho_{mix}} = \frac{W'_{EtOH}}{\rho_{EtOH}} + \frac{W'_{suc}}{\rho_{suc}} \qquad [5.1.1]$$

Where ρ_{EtOH} and ρ_{suc} are the density of aqueous binary solvents and W'_i the weight fraction of component i in the mixture, on a water-free basis.

The dielectric constant of the mixed solvent solution is calculated as the weighted average of dielectric constant of the aqueous binary solvent mixtures.

$$\epsilon_{mix} = \epsilon_{EtOH} W_{EtOH}' + \epsilon_{suc} W_{suc}' \qquad [5.1.2]$$

Where ϵ_{EtOH} and ϵ_{suc} are the dielectric constants of the aqueous ethanol and aqueous sucrose solvents.

The Brønsted-Guggenheim parameter (β) in the ternary solvent mixture is calculated using a similar expression based on the value of β in the two aqueous binary solvent mixtures:

$$\beta_{mix} = \beta_{EtOH} W_{EtOH}' + \beta_{suc} W_{suc}' \qquad [5.1.3]$$

The predicted behavior of a quaternary solution calculated using the parameters determined from the binary and ternary solutions (Tables 4.1,4.2 and 4.3) is shown in Figure 5.1.

5.2 Solubility of Terpenes in Mixed Aqueous Solutions

The distribution of essential oil components between phases during the processing of food solutions is an important parameter affecting the organoleptic quality of the processed foods involved. Terpenes are unsaturated hydrocarbons which occur in most essential oils (Hawley, 1981). The solubility of three of these compounds, carvone, piperitone and pulegone in water (Smyrl and Le Maguer, 1980) and in aqueous solutions of glucose, sucrose and sodium chloride (Smyrl, 1977; Smyrl and Le Maguer, 1980) are available. Solubility data may be used to estimate activity coefficient in saturated solutions. Le Maguer(1981) presents

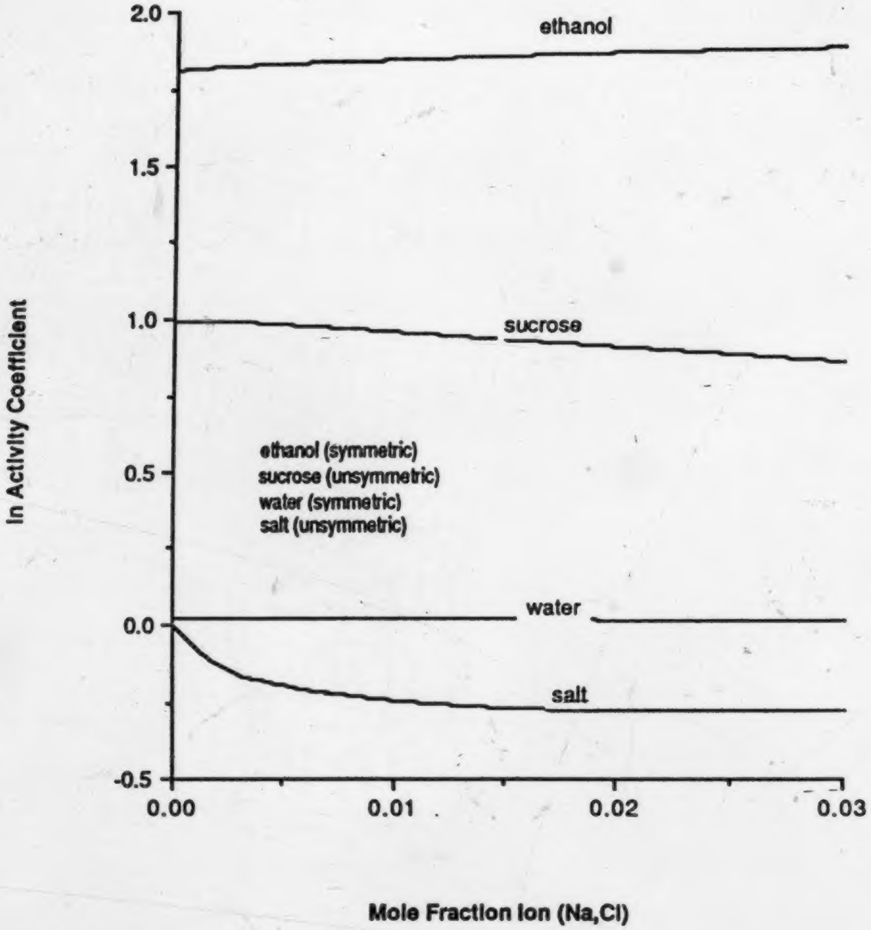

Figure 5.1 Predicted (-) activity coefficients in the quaternary system at 25°C : Solvent Composition : 8.6 mol % Ethanol 1.1 mol % sucrose.

estimates of the saturation activity of the three terpenes at different temperatures. These values, along with the relationships developed in Appendix 4, were used to estimate the terpene activity coefficients in the saturated solutions at 23°C.

Le Maguer (1981) adapted the UNIQUAC equation to the modeling of the terpene-water system and presents temperature dependent expressions for the UNIQUAC interaction parameters in binary, aqueous solutions of these compounds. In the aqueous sucrose system, the application of the extended UNIQUAC equation requires the estimation of two parameters representing the interaction between the sucrose and terpene molecules and between two terpene molecules. The terpene-terpene interaction was assumed to be equal to the ethanol-ethanol interaction and only the terpene-sucrose interaction parameter was required. The effect of the variation of this parameter on the predicted saturation activity coefficient of carvone in aqueous sucrose solution at 20°C is shown in Figure 5.2. This parameter has a significant effect on the calculated carvone activity coefficient. An optimal value of 425 K was estimated for the carvone-sucrose interaction parameter. The activity coefficients of saturated solutions of piperitone and pulegone in aqueous sucrose solutions were also predicted. These components are very similar in structure to carvone, and it was assumed that the energies of interaction of piperitone-sucrose and pulegone-sucrose are equal to

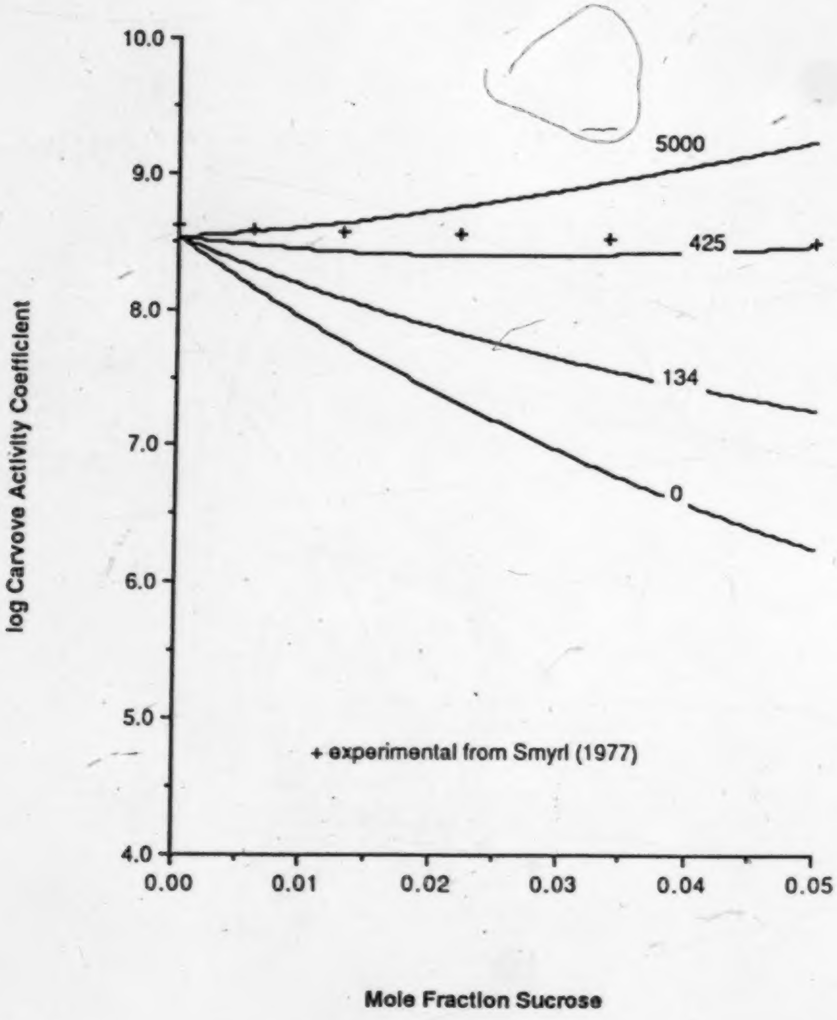

Figure 5.2 Effect of U(carvone-sucrose) on the predicted saturation activity coefficient of Carvone in aqueous sucrose solutions at 23°C. Expt. data adapted from Smyrl (1977)

interaction energy of carvone-sucrose. The predicted and experimental terpene, saturation activity coefficents of pipertone and pugelone in aqueous sucrose are shown in Figures 5.3 and 5.4. As these figures illustrate, the activity coefficients are predicted well with the extended UNIQUAC equation using this parameter value.

The solubility of the terpenes in the aqueous phase are in the order of .00001 on a mole fraction basis (Smyrl, 1977). Because of their low concentrations, the effect of these components on the Brønsted-Guggenheim parameter (β) in aqueous sodium chloride solutions was assumed to be negligible. In a preliminary investigation, the carvone-sodium chloride-water system, the carvone-sodium ion interaction parameter was found not to be significant and set to zero. The effect of the variation of the carvone-chloride ion interaction parameter on the carvone activity coefficient at saturation in solutions of aqueous sodium chloride, is shown in Figure 5.5. As this figure illustrates, the chloride ion has a drastic effect on the carvone activity coefficient. This effect however, cannot be reflected by the extended UNIQUAC equation regardless of the value of the interaction parameter used. Similar results were found for piperitone and pulegone.

The severe salting-out effect of the salt on the terpene is due to very strong interactions between the ions and terpene molecules. Examination of the contributions to the carvone activity coefficient showed this quantity to be

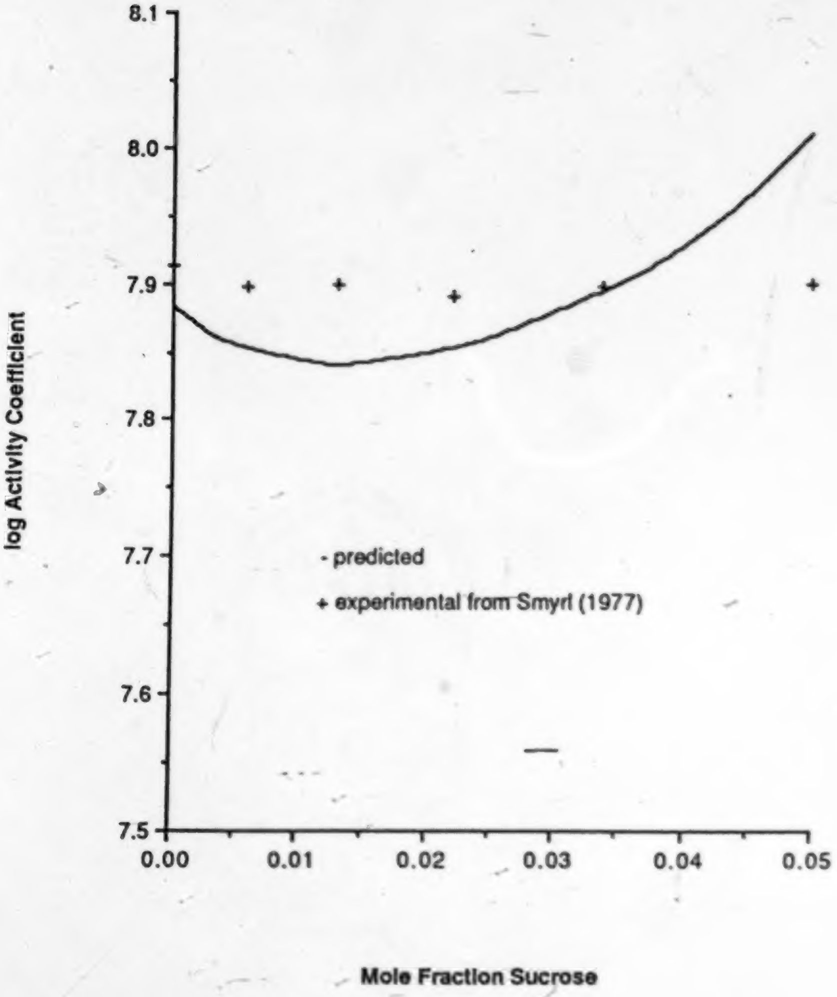

Figure 5.3 Predicted (-) and experimental saturation activity coefficient of Piperitone in aqueous sucrose solutions at 23°C. Expt. data adapted from Smyrl (1977)

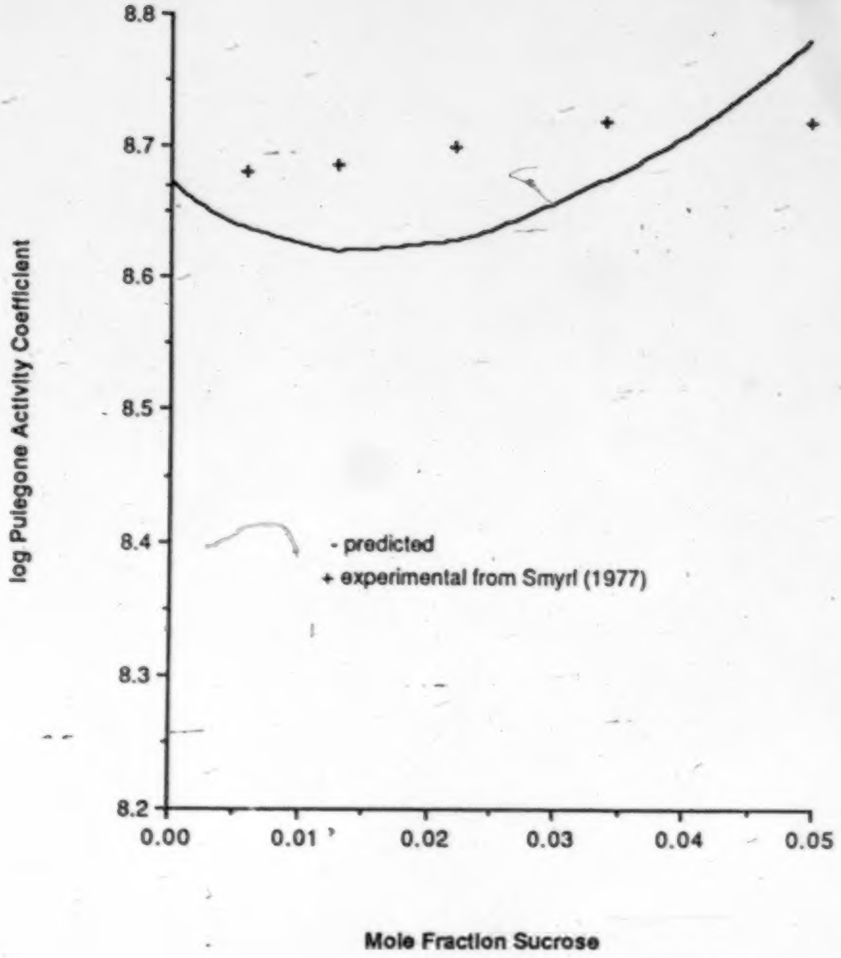

Figure 5.4 Predicted (-) and experimental saturation activity coefficient of Pulegone in aqueous sucrose solutions at 23°C. Expt data adapted from Smyrl (1977)

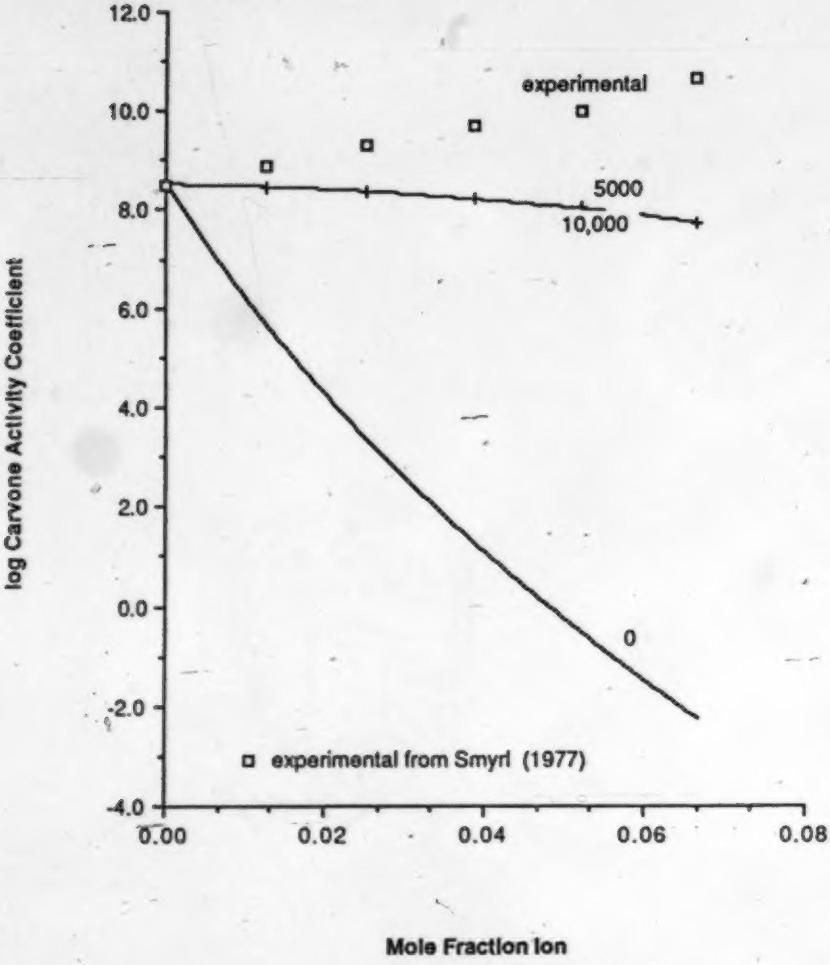

Figure 5.5 Effect of U(carvone-chloride) on the predicted saturation activity coefficient of Carvone in aqueous salt solutions at 23°C. Expt. data adapted from Smyrl (1977)

determined primarily by the UNIQUAC term in the equation. The decrease in the solubility of the terpenes with the addition of sodium chloride and the corresponding increase in the saturation activity coefficients, was reflected properly in the residual term of the equation. This behavior validated the interaction parameters (U_{ij}) used for this system. The inability of the model to properly reflect the severe salting-out effect, was thought to be due to an improper representation of the structure of the solution, or more precisely, the surface area fraction. The representation of the strong interactions between the ions and terpenes are limited by the relatively small value of the cation surface area parameter (q_k). It is believed that this value does not properly reflect the solution structure and as a consequence the local surface area fraction is incorrect and the full extent of the ion-terpene interaction is not represented. Similar problems with the cation geometric parameters were experienced by Sander *et al.* (1986a) in their representation of vapour-liquid equilibria in mixed solvent/electrolyte systems.

5.3 Physical Property Estimation

Physical properties of solutions, such as freezing point depression, solubility, boiling point elevation and relative volatility are based on the phase equilibria of the liquid solution and a second phase, either solid or vapour. With the extended UNIQUAC equation, access to the thermodynamic behavior of each component in the solution is available. Based on this information, the phase equilibrium behavior of the system and a number of analogous physical properties were estimated.

5.3.1 Fugacity as a criterion for equilibrium

The conditions for equilibrium between phases in a multicomponent system at constant temperature and pressure require that the chemical potential of any component i, be equal in all phases in equilibrium (Hougen *et al.*, 1954). The fugacity of a component (f_i) is directly related to its chemical potential (μ_i) at constant temperature by the relationship.

$$\mu_i = \mu_i^o + RT \left[\ln \frac{f_i}{f_i^o} \right] \qquad [5.3.1]$$

Where μ_i^o and f_i^o are the standard state chemical potential and fugacity of component i. Consequently, fugacity may be used as a criterion for equilibrium between phases. For the equilibrium of component i among various phases:

$$f_{i,l} = f_{i,l'} = f_{i,v} = f_{i,s} \qquad [5.3.2]$$

where the subscripts denote different phases. Using Gibbs definition of the activity as the ratio of the component fugacity to its fugacity in a standard state (f_i^o), the equilibrium condition (5.3.2) may be written alternately as

:

$$a_{i,l}f^{o}_{i,l} = a_{i,l'}f^{o}_{i,l'} = a_{i,v}f^{o}_{i,v} = a_{i,s}f^{o}_{i,s} \qquad [5.3.3]$$

where $a_{i,l}$, $a_{i,l'}$, $a_{i,v}$ and $a_{i,s}$ are the activity of component i in phases l,l',v, and s. Based on these relationships and a number of thermodynamic relationships between the standard states, a number of physical properties of solutions may be estimated.

5.3.2 Freezing point depression

The freezing point of a solvent defines the temperature at which equilibrium is established between the solid and liquid states and the solvent fugacities in each phase are equal. This equilibrium state expressed in terms of solvent activities depends only on the relationship between the standard state fugacities in each phase (Prausnitz *et al.*, 1986). When a solute is added to the solvent and dissolves only in the liquid phase, the fugacity of the liquid solvent is lowered. To re-establish equilibrium, the fugacity of the solid solvent must also be lowered. This is achieved by decreasing the solution temperature, noting that the fugacity of the liquid solvent also decreases with the temperature. The magnitude of the temperature decrease required to re-establish equilibrium is the freezing point depression (Klotz, 1964). The variation of the solid activity (a_s) with temperature at constant pressure is given by the relationship:

$$\left.\frac{d\ln a_s}{d\,T}\right]_P = \frac{\Delta H_f}{RT^2} \qquad [5.3.4]$$

Where ΔH_f is the enthalpy of fusion. If the solvent is water, the water activity is related to the freezing point depression (θ_f) by the following relationship (Wall,1958).

$$-\ln a_s = 9.6916\mathrm{x}10^{-3}\theta_f + 4.95\mathrm{x}10^{-2}\theta_f^{\,2} \qquad [5.3.5]$$

The freezing point depression θ_f is defined as : $\theta_f = (T_f^0 - T_f)$ where T_f^0 is the freezing point of the pure solvent under the same pressure and T_f is the freezing point of the solution. Detailed derivations of these relationships are given by Wall (1958) and Lewis and Randall (1961).

With the extended UNIQUAC equation, the water activity of the solution at different temperatures and compositions can be calculated. The temperature at which equation 5.3.5 is satisfied will allow the estimation of the freezing point depression of a given solution. It should be noted that it is assumed that pure ice is precipitated in the solid state.

This relationship has been used to calculate the freezing point depression in aqueous sucrose solutions. The predicted and experimental values are given in Figure 5.6. Experimental freezing point depression measurements are from Honig (1953). As this figure illustrates, this property is predicted well using the extended UNIQUAC equation with an

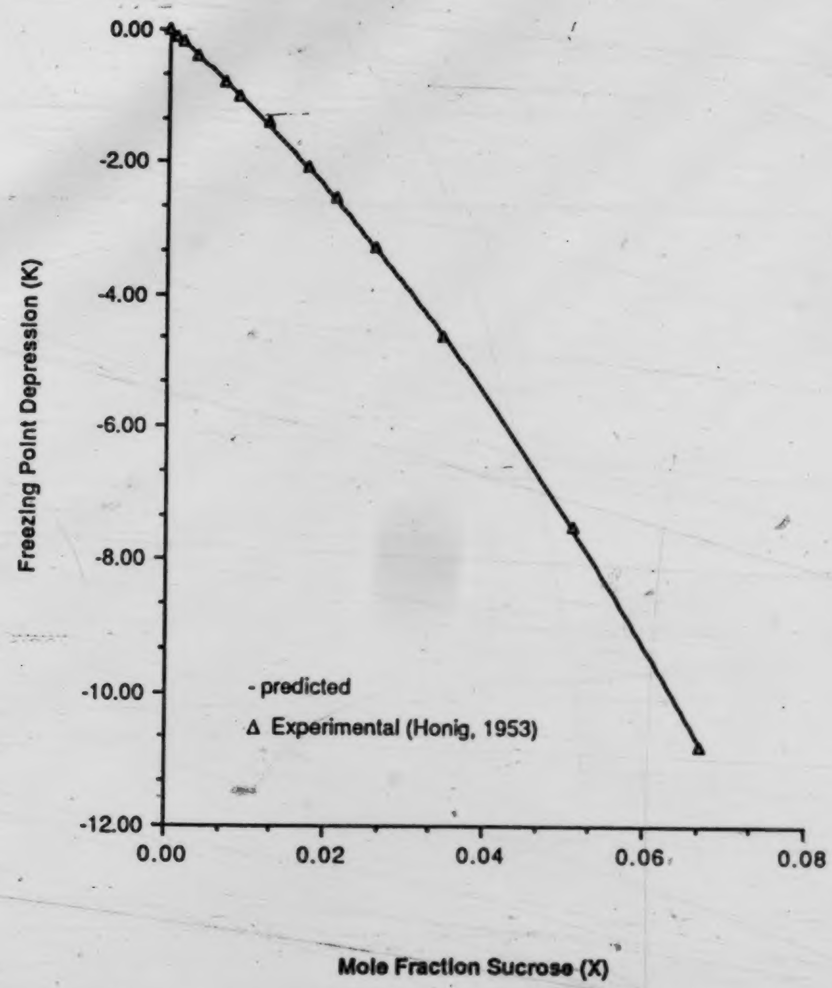

Figure 5.6 Predicted (-) and experimental freezing point depression of aqueous sucrose solutions. Predicted values calculated with eqn. 5.3.5. Expt. data from Honig (1953)

average error on the freezing point depression of less than 2%.

5.3.3 Boiling point elevation

The calculation of boiling point elevation in multicomponent solutions is based on solvent vapour-liquid equilibria. It usually involves aqueous solutions of non-volatile components. The relationship is analogous to that used in the calculation of freezing point depression with the standard state fugacities being related through the molar enthalpy of vaporization of the solvent. For a detailed derivation the reader is referred to the monographs of Wall (1958) and Lewis and Randall (1961).

When the solvent in the solution is water, the vapour phase activity (a_v) is related to the boiling point elevation (θ_b) by the following relationship (Wall, 1958):

$$-\ln a_v = 3.5122\times10^{-2}\theta_b + 7.832911\times10^{-5}\theta_b{}^2 \qquad [5.3.6]$$

The boiling point elevation (θ_b) is calculated as: $\theta_b=(T_b-T_b^0)$. where T_b is the solution boiling point and T_b^0, the boiling point of the pure solvent.

This relationship is used with the extended UNIQUAC equation to predict the boiling point elevation of aqueous sucrose solutions. The predicted and experimental boiling point elevation of aqueous sucrose solutions under atmospheric pressure are presented in Figure 5.7. The

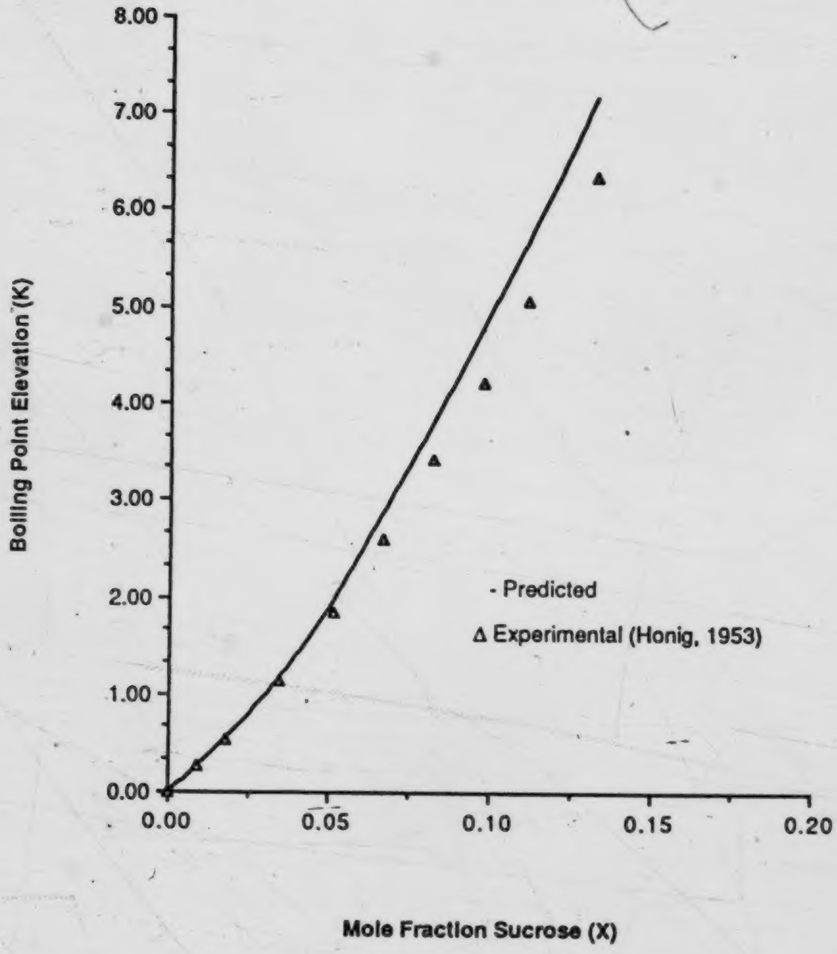

Figure 5.7 Predicted (-) and experimental boiling point elevation of aqueous sucrose solutions. Predicted values calculated with eqn. 5.3.6. Expt. data from Honig (1953)

experimental values are those of Honig (1953). The boiling point elevation is predicted well in the low concentration range. At higher sucrose concentrations, the prediction is not as good. The inability of the model to predict the boiling point elevation in this range is due to the extrapolation of the UNIQUAC parameters to temperatures and concentrations beyond the range in which they were estimated. Typically these parameters may be extrapolated to 20°C on either side of the fitted temperature range. In this application, these values must be extrapolated more than 40°C beyond this range.

The subroutine used to estimated both the freezing point depression and boiling point elevation in the model food solution is presented in Appendix 6.

5.3.4 Solute solubility

1)Sucrose

The relationships between the solid and liquid states in saturated solutions of sucrose developed in Appendix 4, were used to estimate the variation of the sucrose solubility with temperature in the aqueous sucrose system. The predicted and experimental sucrose solubilities over the the temperature range 260-360 K are shown in Figure 5.8. The experimental solubilities are those reported by Honig (1953).

The solubility limit of aqueous sucrose is predicted well using the extended UNIQUAC equation up to a temperature

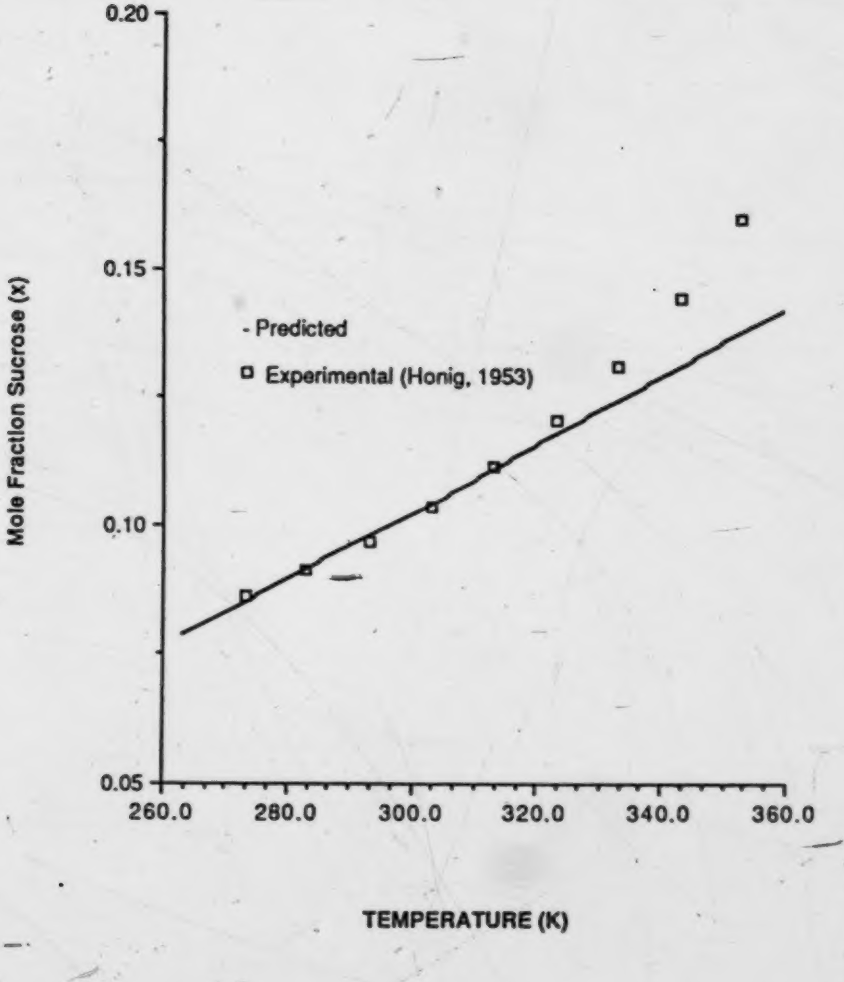

Figure 5.8 Predicted (-) and experimental sucrose solubility in aqueous solutions. Predicted values calculated with eqns. 11.4.1 and 11.4.2 Expt. data from Honig (1953)

of 330 K above this temperature, the prediction is not as good. The average error over the entire range is 14%. Young and Jones (1949) and Chandrasekaran and King (1971) report the sucrose solid-liquid phase diagram under atmospheric pressure and show that above 278 K the solid phase is anhydrous sucrose. The formation of hydrates in the solid phase is therefore, not a reasonable explanation for the inaccurate prediction of the experimental data in the higher temperature range. The inability of the extended UNIQUAC equation to correctly predict the solubility of sucrose in this temperature range is due to both the assumption of constant infinite heat of dilution over the entire temperature range and the extrapolation of the optimized parameters far beyond the range in which they remain reliable. In addition to this, the solubilities are not predicted well in solutions of very high sucrose concentration. This range of concentration is not of great importance in many food processing applications and was not included when the parameter estimation was performed.

2) Sodium Chloride

The solubility of sodium chloride in aqueous solution was studied by Chen (1986). In this work, the solid-liquid equilibria of aqueous electrolytes was predicted using the electrolyte-NRTL model (Chen *et al.*, 1982; Chen and Evans,1986). Using an analysis similar to that presented for sucrose, Chen predicted the solubility of aqueous sodium chloride over the temperature range : 273 - 473 K. The

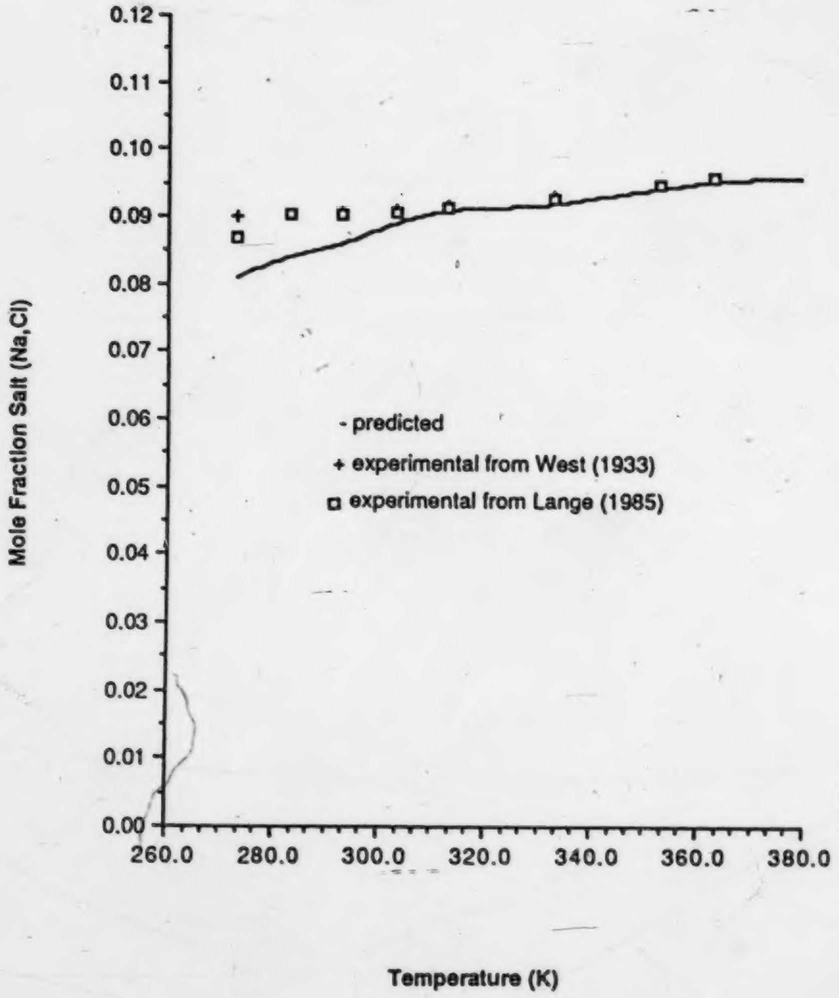

Figure 5.9 Predicted (-) and experimental sodium chloride solubility in aqueous solution. Predicted values calculated with eqns. 5.3.7 and 11.4.1. Expt. data from Lange (1985) and West (1933)

variation of the sodium chloride saturation activity with temperature was fitted as a function of the system temperature from experimental data. The equation has the following form (Chen, 1986):

$$\ln a_s^* = -84.669+\frac{355.94}{T} -16.2296 \ln(T)-0.045253\ T \quad [5.3.7]$$

Where T is the system temperature (K). This expression is used to calculate the variation of the sodium chloride saturation activity with temperature. It was used with the extended UNIQUAC equation to predict the solubility of sodium chloride in aqueous solutions over the temperature range: 260 - 360 K. As Figure 5.9 illustrates, these values are predicted quite well over the entire temperature range with an average error of less than 10%. The experimental data are from Lange (1985) and West (1933).

3) Mixtures of Sucrose and Sodium Chloride

The solubility of sucrose and sodium chloride in ternary mixtures with water were predicted using the previously mentioned relationships and the extended UNIQUAC equation. Figure 5.10 shows the predicted and experimental solubilities of sucrose and sodium chloride in this system at 298.15 K. It can be seen that the solubilities are predicted well in the low concentration range. At higher concentrations, the predicted solubilites are not acceptable. In this concentration region it is believed that the solid phase is not the anhydrous solute. Gayle and his

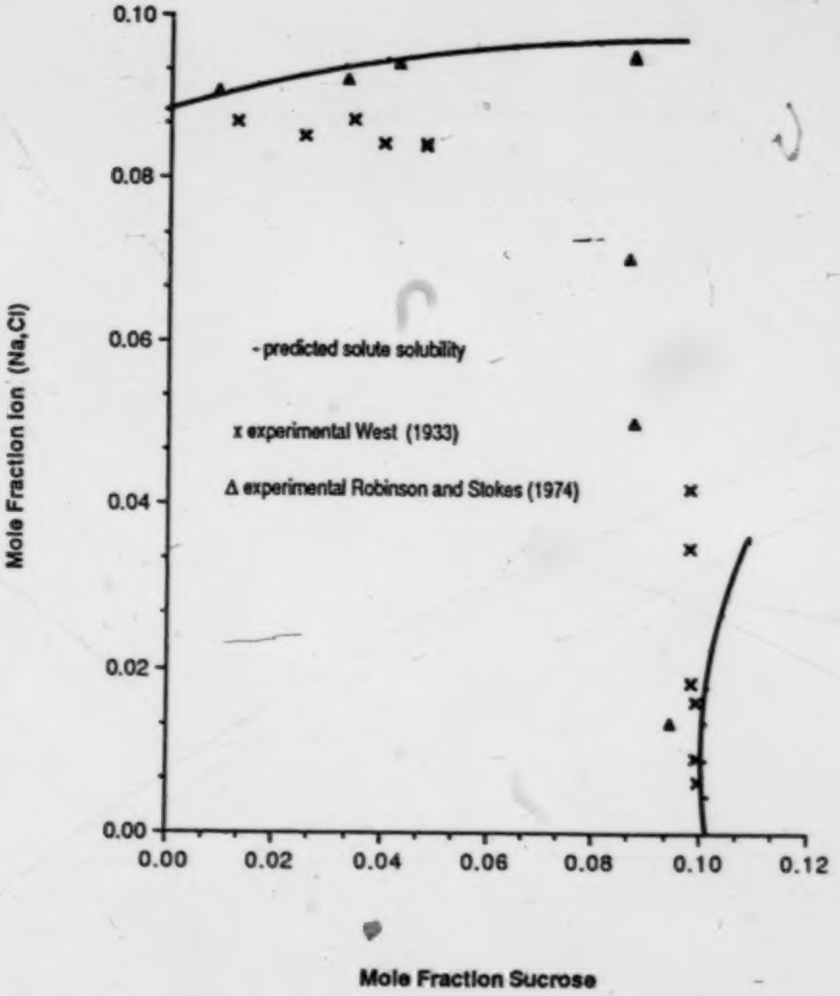

Figure 5.10 Predicted (-) and experimental solubilities in ternary solutions of sodium chloride; sucrose and water at 25°C. Expt. data from Robinson *et al.* (1970) and West (1933)

colleagues (1977) studied the water-NaCl-sucrose phase diagram and report the formation of metastable glassy phases. The degree of metastability of these phases was found to increase with sucrose concentration. They also report the formation of a sodium chloride hydrate at 30°C. The formation of co-precitates and hydrates in this region of concentration are reported by Robinson and his coworkers (1970) and elsewhere in the literature (West, 1933). From the standpoint of testing the validity of the predicted activity coefficients, this is a very severe test illustrating well the accuracy of the predicted solute activity coefficients.

The subroutines developed for the calculation of the solubily of sucrose and sodium chloride in the model food solution are presented in Appendix 6.

5.3.5 Vapour-liquid equilibria

The addition of a non-volatile solute to a mixed solvent consisting of two or more volatile components may have the effect of altering the relative activities of the volatile components (Furter, 1977). The effect of the solute may be due to the formation of liquid-phase associations or complexes. If the dissolved solute associates preferentially with one component of the solvent over the others, the solubility of the volatile components may be altered in such a way that one component is said to be "salted out" with respect to the others. In such systems, the activities of the volatile components are altered relative to one another resulting in a change in the vapour-liquid equilibria of the system, although no solute is present in the vapour phase (Furter and Cook, 1967). Components for which the vapour compositions are enhanced are said to have been "salted out" by the solute, while components for which the equilibrium vapour compositions are decreased are "salted in" (Furter, 1977). This effect is exploited in the extractive distillation of difficult systems such as those of low relative volatilities or systems exhibiting azeotropic behavior in composition regions critical to the separation (Furter and Cook, 1967).

The vapour-liquid equilibrium relationships developed in Appendix 4 were used with the extended UNIQUAC equation to predict the effect of sodium chloride on the isobaric equilibrium vapour-phase composition of aqueous ethanol solutions. Figure 5.11 shows the predicted and experimental vapour phase compositions of aqueous ethanol solutions saturated with sodium chloride, under atmospheric pressure. The salting-out effect of the sodium chloride on the ethanol is predicted well as this figure illustrates. This effect is particularly strong in the dilute ethanol concentration region, where the solubility of the salt in the solution is appreciable.

Figure 5.12 shows the predicted salting out effect of sucrose on the ethanol-water system under atmospheric pressure. Experimental vapour-liquid equilibrium data on

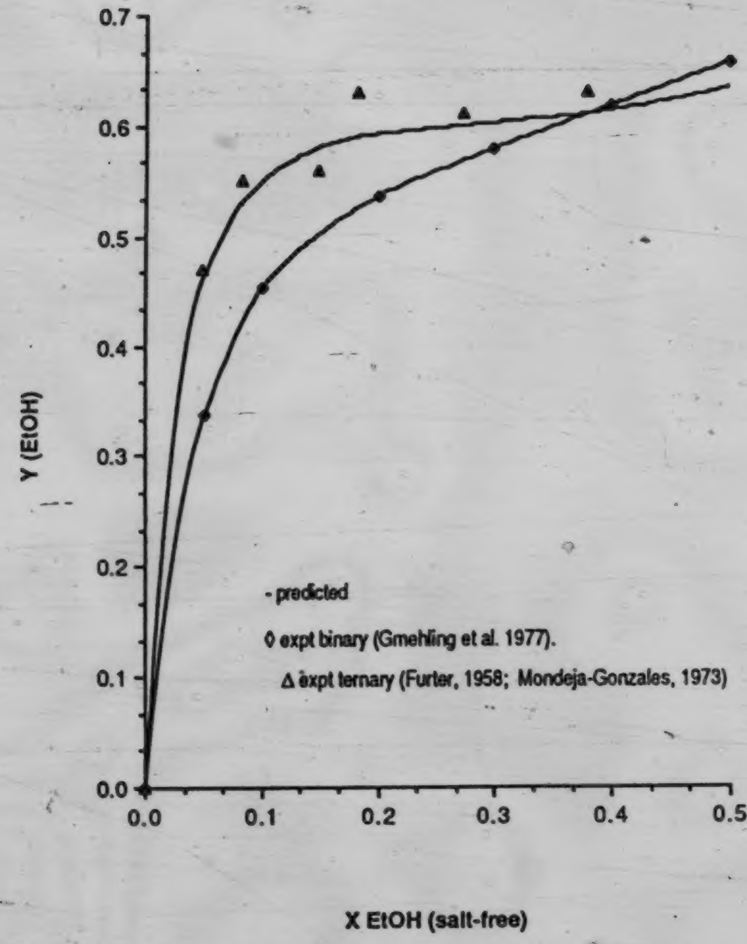

Figure 5.11 Predicted (-) and experimental vapour-liquid equilibria in aqueous ethanol saturated with NaCl at 760 mm Hg. Values calculated with eqns. 11.2.1 and 11.2.2. Expt. data from Furter (1958) and Mondez-Gonzalez (1973)

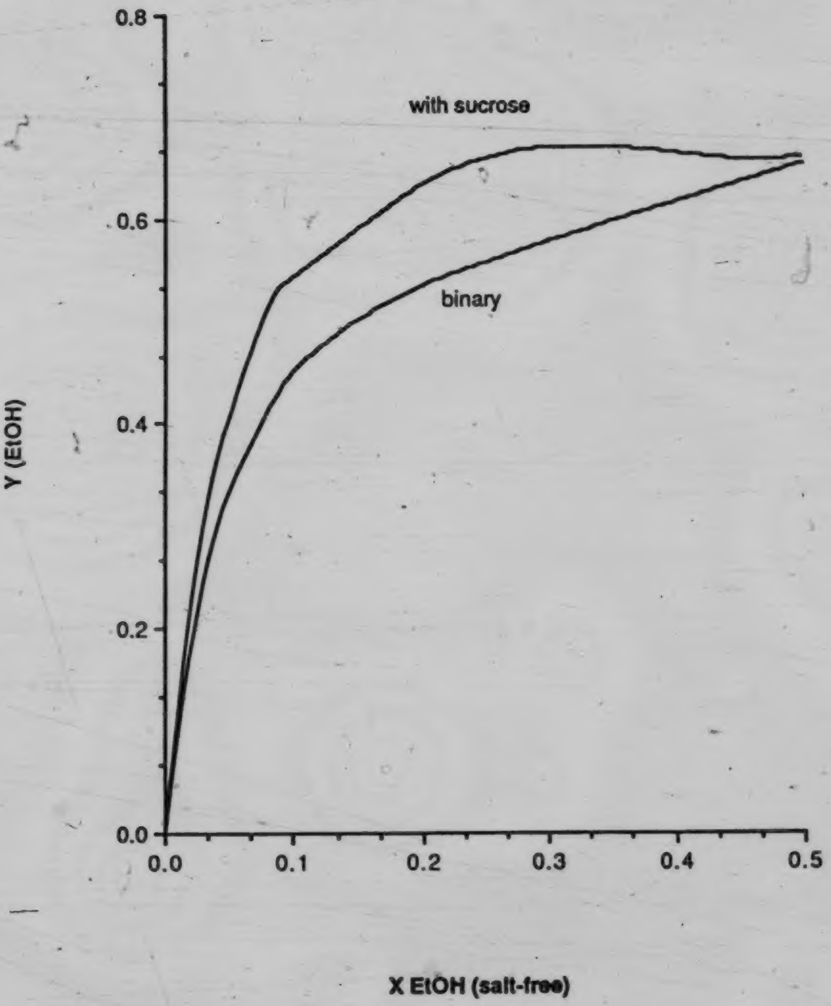

Figure 5.12 Predicted (-) salting-out effect in aqueous ethanol solutions saturated with sucrose at 760 mm Hg. Predicted values calculated with eqns. 11.2.1 and 11.2.2.

this system are not available in the literature, however, Sorrentino and his colleagues (1986) in their studies of aroma compounds in model food solutions, found ethanol to be salted-out by glucose and maltose in ternary ethanol-carbohydrate-water systems.

The subroutine developed for the prediction of equilibrium vapour-phase compositions in the model food system is presented in Appendix 6.

5.4 Mass Transfer

The applications of the extended UNIQUAC equation presented thus far are based on classical thermodynamic relationships. For non-equilibrium processes, classical thermodynamics makes only general statements about the direction of change. (Katchalsky, 1967). The extended UNIQUAC equation may be applied to transient, irreversible processes with the assumption of local equilibrium.

Over a century ago the flow of slow, irreversible processes was found to be directly proportional to their driving forces (Katchalsky, 1967). Examples of this relationship include Fourier's law of heat transfer, Ohms law for electrical flow and Fick's law of diffusion. The extended UNIQUAC equation may be used to predict chemical potential driving forces and in combination with an extended form of Fick's law, to describe mass transfer processes. Fick's law is restricted to systems near equilibrium in which a linear dependency of flows with their conjugate driving forces is exhibited. In many cases however, coupled flows are known to exist with the flows also dependent on the non-conjugated forces (Kachalsky, 1963). Attempts to describe such phenomea in terms of linear dependency has lead to misunderstanding of the processes involved.

The phenomenological approach to the description of diffusional flows takes into account the dependency of the flows on the non-conjugate forces. In this treatment, the dependency of flows on different driving forces are not necessarily linear and thus accurate descriptions of the driving forces are vital, if the correct dependencies are to be derived. This approach may be used to describe transmembrane mass transfer in both biological systems and in the growing field of membrane separation techniques.

Guenneugues (1986) studied the osmotic dehydration of carrot tissue in aqueous sodium chloride solutions using a thin packed bed. The phenomenological approach was used to model the mass transfer in this system. The component fluxes were described using the following equations:

$$J_w=K_{w,w}\frac{\Delta\mu_w}{T}+K_{w,s}\frac{\Delta\mu_s}{T}+K'_{w,w}\frac{\Delta\mu_w}{T}^2+K'_{w,s}\frac{\Delta\mu_s}{T}^2+K''_{w,s}\frac{\Delta\mu_w}{T}\frac{\Delta\mu_s}{T} \qquad [5.5.1]$$

$$J_s=K_{s,s}\frac{\Delta\mu_s}{T}+K_{s,w}\frac{\Delta\mu_w}{T}+K'_{s,s}\frac{\Delta\mu_s}{T}^2+K'_{s,w}\frac{\Delta\mu_w}{T}^2+K''_{s,w}\frac{\Delta\mu_s}{T}\frac{\Delta\mu_w}{T} \qquad [5.5.2]$$

Where J_i represents the flux of component i, $K_{i,j}$ are mass transfer coefficients and $\Delta\mu_i$ is the chemical potential gradient for mass transfer. To represent these driving forces, Guenneugues used the extended UNIQUAC equation. The effect of other solutes in the tissue on the gradient was taken into account by representing all the soluble solutes in the carrot as an equivalent sucrose concentration. The chemical potentials required in equations 5.5.1 and 5.5.2 were calculated inside the carrot based on a ternary sodium chloride-sucrose-water system. Initially, the outer bath was assumed to be a binary sodium chloride-water solution.

The design of processes for biological fluids requires descriptions of the physical properties of the components involved. It is also essential to have a description of the product behavior under different conditions of temperature and ionic strength (Johnson, 1986). The description of mass transfer driving forces are also required for the design of mass transfer operations, particularily if the phenomenological approach is used to describe the mass transfer.

6. CONCLUSIONS AND RECOMMENDATIONS

In this study, the extended UNIQUAC equation proposed by Christensen *et al.* (1983) was modified and applied to an aqueous system containing ethanol, sucrose and sodium chloride. With the modified version of the equation, the activity coefficients of the aqueous ternary and binary subsystems were represented well.

The van der Waals derived volume and surface parameters for sucrose did not accurately represent the the sucrose molecule in aqueous solution. With the modified values of these parameters, both activity coefficients and partial molar enthalpies of this system were represented well, over the 0-6 molal sucrose concentration range and the 0-60°C temperature range. The %RMSD (% Root Mean Square Deviation) of the component activity coefficients being 6.6%. Based on the estimated activity coefficients, freezing point depression, boiling point elevation and sucrose solubility in the system were predicted very accurately. Discrepancies in the predicted properties were only observed in highly concentrated solutions.

Component activity coefficients in solutions of sodium chloride in aqueous ethanol were predicted well with the equation to salt concentrations up to saturation. The average %RMSD of the solvent activity coefficients in solutions saturated with salt was 8.5%, while the salt activity coefficients were predicted with an average %RMSD of 11%. The salt activity coefficients in the dilute concentration range were not correlated well indicating that the electrostatic interactions were not correctly represented in the equation. The predicted solvent activity coefficients were validated with the prediction of the system equilibrium vapour composition. This composition was predicted with an average %RMSD of 6.3%.

The solute activity coefficients in the ternary sucrose-sodium chloride-water system were correlated accurately with the extended UNIQUAC equation. The average %RMSD of the salt and sucrose activity coefficients were 8 and 5% respectively. Solubilities of the two solutes in the ternary system were predicted accurately based on the predicted activity coefficients in the low to moderate concentration range.

The solubility behavior of three terpenes in aqueous sucrose solutions was represented well with the equation based on the estimation of a single parameter. The effect of sodium chloride on the solubility behavior of these components could not be represented by the equation.

6.1 Recommendations

This study has revealed a general need for consistent and complete thermodynamic data on the selected system and its sub-systems. For a complete validation of the model, experimental activity coefficients and partial molar enthalpy data are required over wide temperature and concentrations ranges.

Experimental activity coefficient and enthalpy data are required for the aqueous sucrose system. Studies on the structure of aqueous solutions of sucrose are also needed to independently validate the geometric parameters of the sucrose molecule estimated in this study.

For the ternary sodium chloride-ethanol-water system, solvent activity coefficients at salt concentrations below saturation are required. To test the predicted temperature variation in this system and the geometric parameters, enthalpy data at different temperatures are also required. Salt activity coefficients at different temperatures would allow a better estimation of the required parameters.

A single source of experimental activity coefficient data at a single temperature was used to estimate the parameters in the aqueous sucrose-sodium chloride system. These parameters should be validated with additional, independent activity coefficient measurements. The predicted variation with temperature and the geometric parameters must also be validated with additional experimental data. Studies on the extent of ion pairing and ion association in this system are also required.

The parameters required for the ethanol-sucrose-water and terpene-sucrose-water systems were estimated based only on solubility data. Experimentally determined activity coefficient data for these systems at concentrations below saturation are needed. Vapour-liquid equilibrium data for these systems would allow validation of the the predicted water activity coefficients.

Studies on the electrostatic interaction between ions in mixed solvent solutions are required to develop a better representation of these interations; of particular importance is the effect of the ions on the solution dielectric constant.

Finally, to validate the predictive powers of the extended UNIQUAC equation, measurements of physical properties which may be predicted based on activity coefficients in the quaternary model solution are required these properties could include freezing points, solubilities or vapour-liquid equilibria.

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8. APPENDIX 1 : The Thermodynamic Representation of Strong Electrolytes in a Mixed Solvent.

In this treatment of mixed solvent/salt systems, the electrolytes are assumed to be completely dissociated. All other components are treated as "solvent" components. The mole fraction of a solvent component (x_s) is defined as:

$$x_s = \frac{n_s}{\Sigma n_m + \Sigma n_j} \qquad [8.1.1]$$

where n is the number of moles, j is summed over all the ions in solution and m over all the solvent components. The mole fraction of ion i (x_i) is given by:

$$x_i = \frac{n_i}{\Sigma n_m + \Sigma n_j} \qquad [8.1.2]$$

Salt-free mole fractions are calculated as:

$$x_s' = \frac{n_s}{\Sigma n_m} \qquad [8.1.3]$$

The molality scale is often used to express concentrations of salts and solutes of limited solubility, giving molal concentrations on the basis of one kilogram of solvent. It is defined as:

$$m_i = \frac{n_i}{\Sigma n_m M_m} \qquad [8.1.4]$$

where M_m is the molecular weight of solvent m expressed in kg mol^{-1}. The relationship between the mole fraction (x_i)

and molality (m_i) is given by (Christensen *et al.*, 1983):

$$x_i = \frac{m_i}{\Sigma m_j + 1/(\Sigma x_m M_m)} \qquad [8.1.5]$$

The chemical potential (μ_s) of a solvent component in mixed solvent/electrolyte solution is defined as:

$$\mu_s = \mu^0_{s\ o} + RT \ln (x_s \gamma_s) \qquad [8.1.6]$$

where $\mu^0_{s\ o}$ is the standard partial molar Gibbs energy of the pure liquid solvent at the temperature and pressure of the system, and γ_s is the symmetric activity coefficient of the solvent component. For ions, expressed on an unsymmetric basis, the chemical potential is calculated as:

$$\mu_i = \mu^*_{i\ o} + RT \ln (x_i \gamma^*_i) \qquad [8.1.7]$$

where $\mu^*_{i\ o}$ is the standard partial molar Gibbs function of solute i on a mole fraction basis, and $\gamma_i{}^*$ is the unsymmetric activity coefficient on a mole fraction basis.

On a molality basis, the definition of the chemical potential is similar:

$$\mu_i = \mu^*_{i\ o,m} + RT \ln (m_i \gamma^*_{i,m}) \qquad [8.1.8]$$

where $\mu^*_{i\ o,m}$ is defined on a molality basis, and $\gamma^*_{i,m}$ is the unsymmetric activity coefficient.

9. APPENDIX 2 : A Review of Standard States and Activity Coefficient Normalization

Some of the thermodynamic concepts important for the application of the extended UNIUQAC equation to the model food systems will be reviewed. This section is included primarily for reference.

9.1 Standard States

The activity of a component (a_i) at a given temperature (T), pressure (P) and composition (x) is defined as the ratio of the component fugacity under the system conditions (f_i) to the fugacity of the component in its standard state (f_i^o) (Lewis and Randall, 1961).

$$a_i(T,P,x) = \frac{f_i\{T,P,x\}}{f_i^o\{T,P^o,x^o\}} \qquad [9.1.1]$$

The selection of the standard state fugacity is arbitrary and based on experimental convenience and reproducibility (Hougen *et al.*, 1954). The temperature of the standard state is the same as the system; the pressure and concentration, however, are arbitrarily chosen at values that may be conveniently measured or accurately calculated. Under certain conditions, the standard state may represent a hypothetical state which cannot be measured experimentally, but may be calculated with reproducible results (Hougen *et al.*, 1954). The standard states selected for use in the thermodynamic representation of the sodium chloride-sucrose-ethanol-water system will be reviewed.

The standard state used for the calculation of the ethanol and water activities is the pure component at the temperature and pressure of the system. Component activity coefficients, calculated in this way, are less than unity and in ideal solutions, are equal to the component mole fractions. Solution ideality is defined by Raoult's law. For some components, this standard state may represent a hypothetical liquid.

This standard state is not practical for application to solutes of limited solubility because it requires experimental data on the pure solute under the system conditions or data on solutions of sufficiently high concentration that Raoult's law might be approached and extrapolated to obtain the fugacity of the pure solute at unit mole fraction. Under normal conditions sucrose exists as a solid and data for it in liquid state are not available.

This standard state may also be estimated from solid-liquid equilibrium data using a thermodynamic cycle. This estimation requires knowledge of the enthalpy or entropy of fusion and is valid only under conditions close to the solute triple point. For details of this procedure, the reader is refered to Prausnitz *et al.*, (1986). This method cannot be used for either the sucrose or sodium chloride in the model food system. Sucrose under normal pressures, decomposes upon heating and consequently data does not exist for its enthalpy or entropy of fusion. The triple point of sodium chloride is far removed from normal temperatures and the estimation procedure is not valid over this wide temperature range (Acree, 1984).

The standard state usually used for solutes of this type is the infinite dilution state. When concentrations are expressed as mole fractions, this state is called the rational standard state. In dilute solutions, where Henry's law is applicable, the solute activity is equivalent to its mole fraction, and free-energy changes may be calculated in terms of the fugacity given by Henry's law (Klotz, 1964). The standard state fugacity is the fugacity the solute would have at unit mole fraction, if Henry's law could be extrapolated to this concentration. Numerically this value is equal to the Henry's law mole-fraction constant, at the temperature and pressure of the system.

For systems in which concentrations are expressed as molalities, the practical standard state, analogous to the rational standard state is used. The standard state fugacity, in this case, is the fugacity the solute would have at unit molality, if Henry's law applied. This value is equal to the Henry's law, molality constant. In both of these standard states, solution ideality occurs in very dilute solutions and is defined by Henry's law.

In solutions of strong uni-valent electrolytes, the limiting behavior of the fugacity at infinite dilution cannot be extrapolated in terms of the salt concentration

(Klotz, 1964). The limiting slope of the fugacity may however, be correlated with respect to the square of the solute concentration. In uni-valent, strong electrolyte solutions, ideal fugacities are determined by Henry's law based on the square of the solute concentration. From the standpoint of dissociation of the ions, the activity is represented by the product of the individual ion activities, as no experimental method exists for the determination of individual ion activities.

9.2 Normalization of Activity Coefficients

The activity coefficient (γ_i) is defined as the ratio of a component activity to the activity observed if the component exhibited ideal behavior. Ideality may be defined either on a Raoult's or Henry's law basis. The choice of standard state leads to different conventions of normalization. For liquid solvents, ideality is usually defined on a Raoult's law basis and the activity coefficient is normalized such that $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$. For such components, as the composition of the solution approaches that of the pure liquid, the fugacity becomes equal to the mole fraction (x_i) multiplied by the standard state fugacity (f_i^o). This normalization convention is termed the symmetric convention of normalization.

Solutions in which the standard state of the solute, is defined by Henry's law are normalized in the following manner:

$$\gamma_i \to 1 \quad x_i \to 1 \text{ (solvent components)}$$

$$\gamma_i^* \to 1 \quad x_s \to 0 \text{ (solute components)}$$

Since the normalization of the system components are not the same, they are said to follow the unsymmetric convention (Prausnitz *et al.*, 1986). In such solutions, the standard state fugacity of the solvent is the pure liquid fugacity and, the solute uses the Henry's law constant.

The Henry's law constants are functions of both the system temperature and the nature of the solvent. This property is the greatest disadvantage of using the Henry's law constants as the standard state fugacities as required by the unsymmetric convention for normalization (Prausnitz *et al.*, 1980).

In binary solutions, activity coefficients (γ_i) which are normalized symmetrically are related to unsymmetric activity coefficients (γ_i^*) by the following relationships (Prausnitz *et al.*, 1986):

$$\frac{\gamma_i}{\gamma_i^*} = \text{limit}_{x_s \to 0}\ \gamma_i \qquad [9.2.1]$$

$$\frac{\gamma_i}{\gamma_i^*} = \text{limit}_{x_s \to 1}\ \gamma_i^* \qquad [9.2.2]$$

In solutions of strong electrolytes, salt activity coefficients are defined using the unsymmetric convention of normalization; this with respect to the salt at infinite dilution. The activity coefficient of each ion approaches unity when the concentration of all ions in solution approaches zero: $\gamma_i^* \to 1$ as $\Sigma x_i \to 0$; this is often called the rational unsymmetric activity coefficient.

On a molality basis, the molal, unsymmetric activity coefficient ($\gamma_{i,m}^*$) is defined as:

$$a_{i,m}^* = \gamma_{i,m}^* m_i \qquad [9.2.3]$$

where $\gamma_{i,m}^*$ is the practical, unsymmetric activity coefficient such that $\gamma_{i,m}^* \to 1$ as $\Sigma m_j \to 0$.

Unsymmetric activity coefficients on a molal and mole fraction basis are related as follows (Sander *et al.*, 1986a):

$$\gamma_i^* = \frac{\gamma_{i,m}^*}{(1 - \Sigma x_i)} \qquad [9.2.4]$$

where the summation is over all the ions.

Single ion activity coefficients are not obtainable from experimental data (Christensen *et al.*, 1983). For an anion-cation pair, the rational mean unsymmetric activity coefficient ($\gamma_\pm^*$) is defined as:

$$\gamma_\pm^* = (\gamma_+^{*\nu+} \gamma_-^{*\nu-})^{1/(\nu+ \nu-)} \qquad [9.2.5]$$

where ν^+ and ν^- are the stoichiometric coefficients of the ions. The practical, mean, unsymmetric activity coefficient ($\gamma_{\pm,m}^*$) is defined similarly. This quantity is the quantity most often tabulated in data collections for electrolyte solutions (Sander *et al.*, 1986a).

10. APPENDIX 3 : Correlation of Solvent Physical Properties

The density and dielectric constant of the solvent mixture is required for the Debye-Hückel limiting law. To estimate these values under different conditions of temperature and pressure, correlations for the density and dielectric constant of the two binary aqueous systems, based on experimental data, were developed.

10.1 Aqueous Ethanol Solutions

Experimental data for the variation of the dielectric constant of aqueous ethanol solutions, with temperature are not widely available. Sen *et al*. (1979) and Harned and Owen (1958) report experimental values at 25°C. Correlations are available for the variation of the pure component dielectric constants with temperature (Weast, 1979). To utilize these correlations, the dielectric constant of the mixture was fitted as a function of the pure component dielectric constants and an excess function. The excess function was fitted as a function of the solution composition at 25°C. Because no data were available for the mixture at different temperatures, it was assumed that the effect of temperature on the excess function was neglible and most of the variation due to temperature was accounted for in the variation of the pure component dielectric constants. The correlation developed for the dielectric constant of aqueous ethanol is given as:

$$\epsilon_{mix} = W_w \epsilon_w + W_{EtOH} \epsilon_{EtOH} - 1.052 W_w W_{EtOH} - 16.89 W_w W_{EtOH}^2 \qquad [10.1.1]$$

Where W_w and W_{EtOH} are the weight fractions of water and ethanol in the solution, ϵ_w and ϵ_{EtOH} are the pure component dielectric constants of water and ethanol at the system temperature, and ϵ_{mix} the dielectric constant of the solvent mixture. The pure component dielectric constants are calculated from the following relationships (Weast, 1979):

Water:

$$\epsilon_{w,t} = 78.54\times10^{(0.05 - (.002*t))} \qquad [10.1.2]$$

Ethanol

$$\epsilon_{EtOH,t} = 24.3\times10^{(0.0675 - (.0027*t))} \qquad [10.1.3]$$

where $\epsilon_{w,t}$ and $\epsilon_{w,t}$ are the pure component dielectric constants at t °C.

Experimental data for the density of aqueous ethanol over a wide temperature range are available in the literature (Perry and Chilton, 1979; Weast, 1979). To estimate the density of aqueous ethanol solutions, a correlation similar to that used for the dielectric constant was developed. Bondi (1968) suggests the use of volume additivity when estimating the densities of multicomponent solutions. Based on this, the following expression was developed to estimate the densities of ethanol-water mixtures:

$$1/\rho_{mix} = W_w/\rho_w + W_{EtOH}/\rho_{EtOH} + 73.85\ W_w\ W_{EtOH} + 415.843\ W_w\ W_{EtOH}^2 - 892.256\ W_w\ W_{EtOH}^3 + 552.202\ W_w\ W_{EtOH}^4 \qquad [10.1.4]$$

where ρ_w and ρ_{EtOH} are the pure component densities at the system temperature and ρ_{mix} is the density of the mixture.

The variation of the density of water with temperature is given by the correlation of (Kell, 1975). The variation of the ethanol density with temperature is fitted as a linear function of the temperature as suggested by Bondi (1968). The density of ethanol in the temperature range 0 - 40°C reported by Weast (1979) is used to estimate this variation. The pure ethanol density is calculated using the following expression:

$$\rho_{EtOH,t} = 806.278 - 0.843*t \qquad [10.1.5]$$

where $\rho_{EtOH,t}$ is the density of pure ethanol at t ° C.

The coefficients in equation 10.1.4 representing the excess volume were estimated based on data at 25°C. The excess volume is a function of temperature. Over the temperature range of interest however, this effect was not significant. The maximum error on the predicted density in the 0 - 100°C temperature range was less than 1% using the coefficients estimated at 25°C. The predicted and experimental density and dielectric constant in aqueous ethanol solutions are given in Figures 10.1 and 10.1.

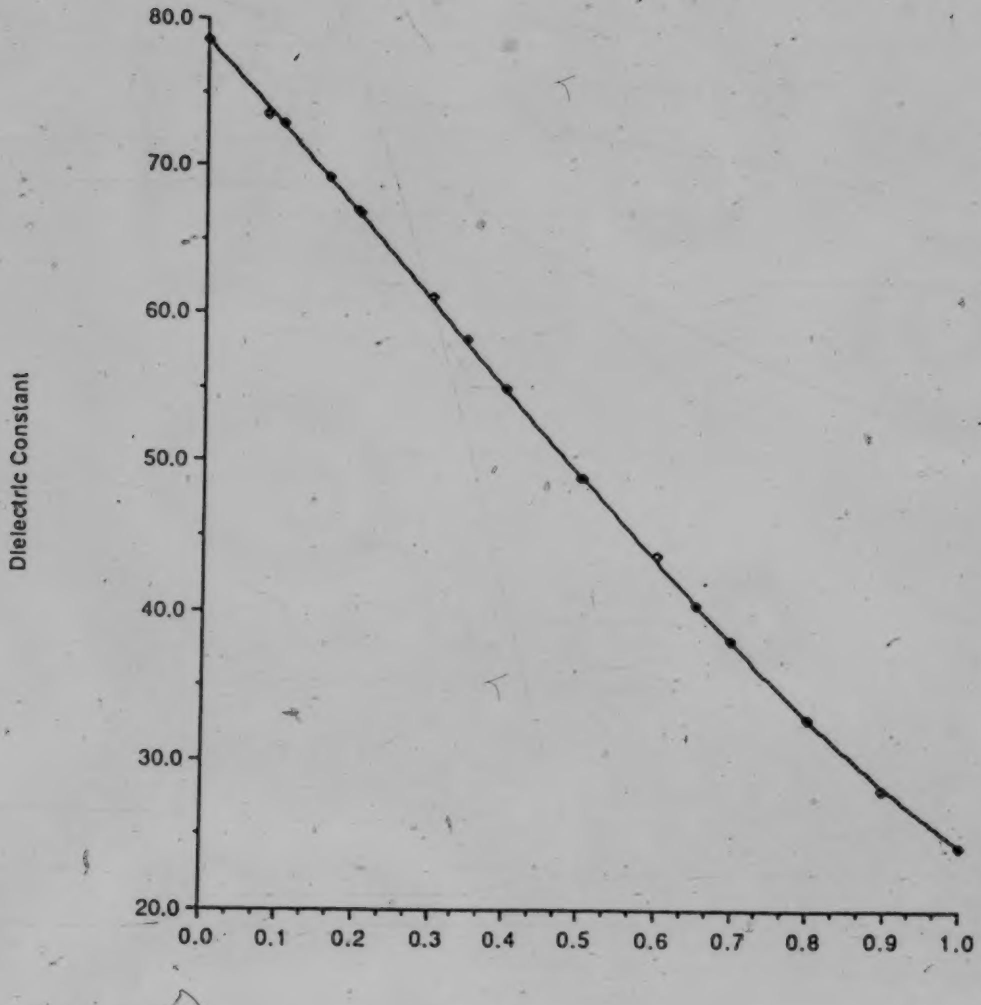

Figure 10.1 Correlation of the dielectric constant of aqueous ethanol at 25°C. Experimental data from Sen *et al.*, (1979) and Harned and Owen (1959).

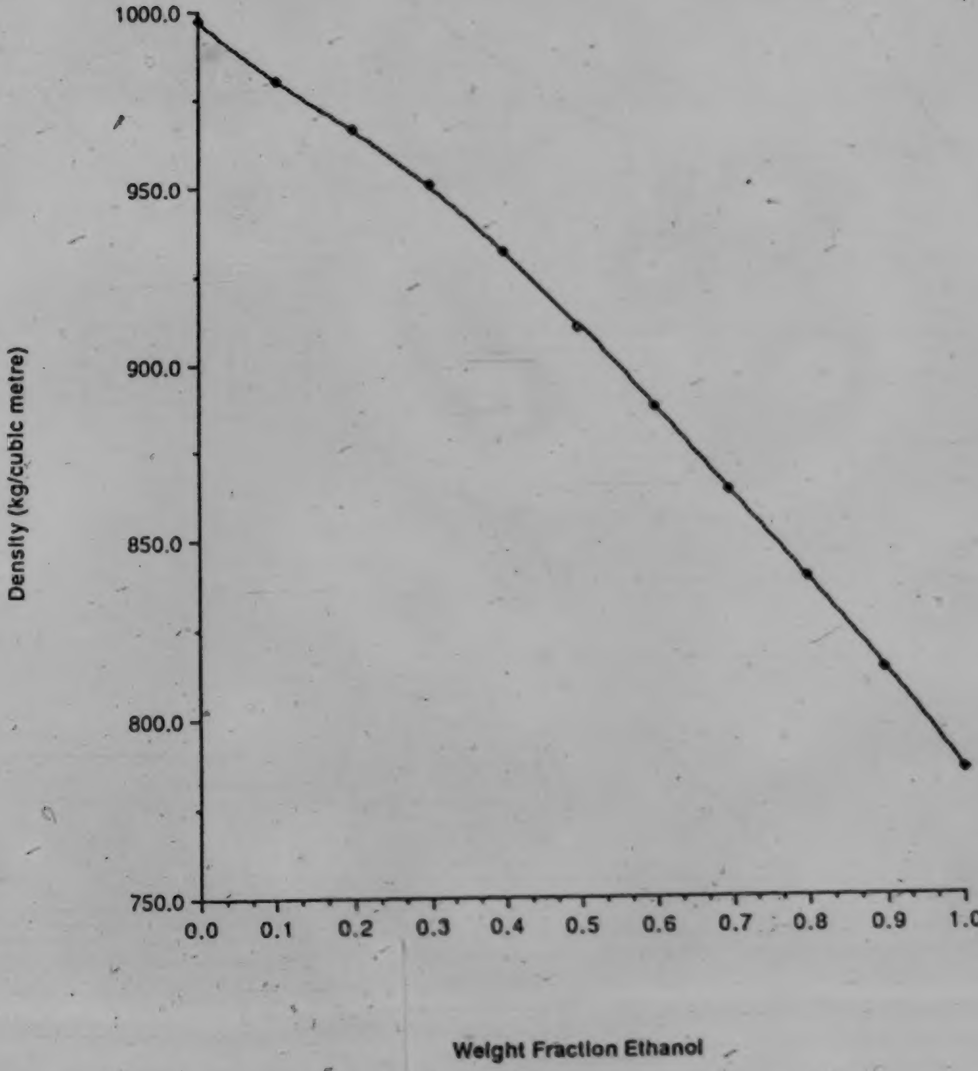

Figure 10.2 Correlation of the density of aqueous ethanol solutions at 25°C. Experimental data from Sen *et al*. (1979) and Weast (1979).

10.2 Aqueous Sucrose Solutions

The density and dielectric constant of aqueous sucrose solutions were fitted as as functions of the solute concentration at 25° The intercepts of the fitted polynomials were forced through the pure water density and dielectric constant. The effect of temperature on the density estimation was assumed to be completely accounted for by the temperature variation of the pure water. To test this assumption, the density of 70 wt % sucrose solutions at 0 and 60°C were predicted using the equation and compared to the experimental densities reported by Honig (1953). The effect of temperature on the density of water was estimated using the correlation of Kell (1975). The maximum error on the predicted densities was found to be less than 1%. This level of accuracy is acceptable for application to the model. The density of aqueous sucrose solutions is estimated using the equation

$$\rho_{mix} = \rho_w + 381.8W_{suc} + 140.6W_{suc}^2 + 33.01W_{suc}^3 \qquad [10.2.1]$$

The dielectric constant of aqueous sucrose solutions is reported at 25°C by Harned and Owen (1958). These data were fitted as a function of solution composition. It was assumed that the effect of temperature on the solution dielectric constant was accounted for in the variation of the pure water dielectric constant. The equation developed is given below:

$$\epsilon_{mix} = \epsilon_w - 25.68W_{suc} + 10.99W_{suc}^2 \quad 34.29W_{suc}^3 \qquad [10.2.2]$$

The predicted and experimental density and dielectric constant in aqueous sucrose solutions are given in Figures 10.3 and 10.4.

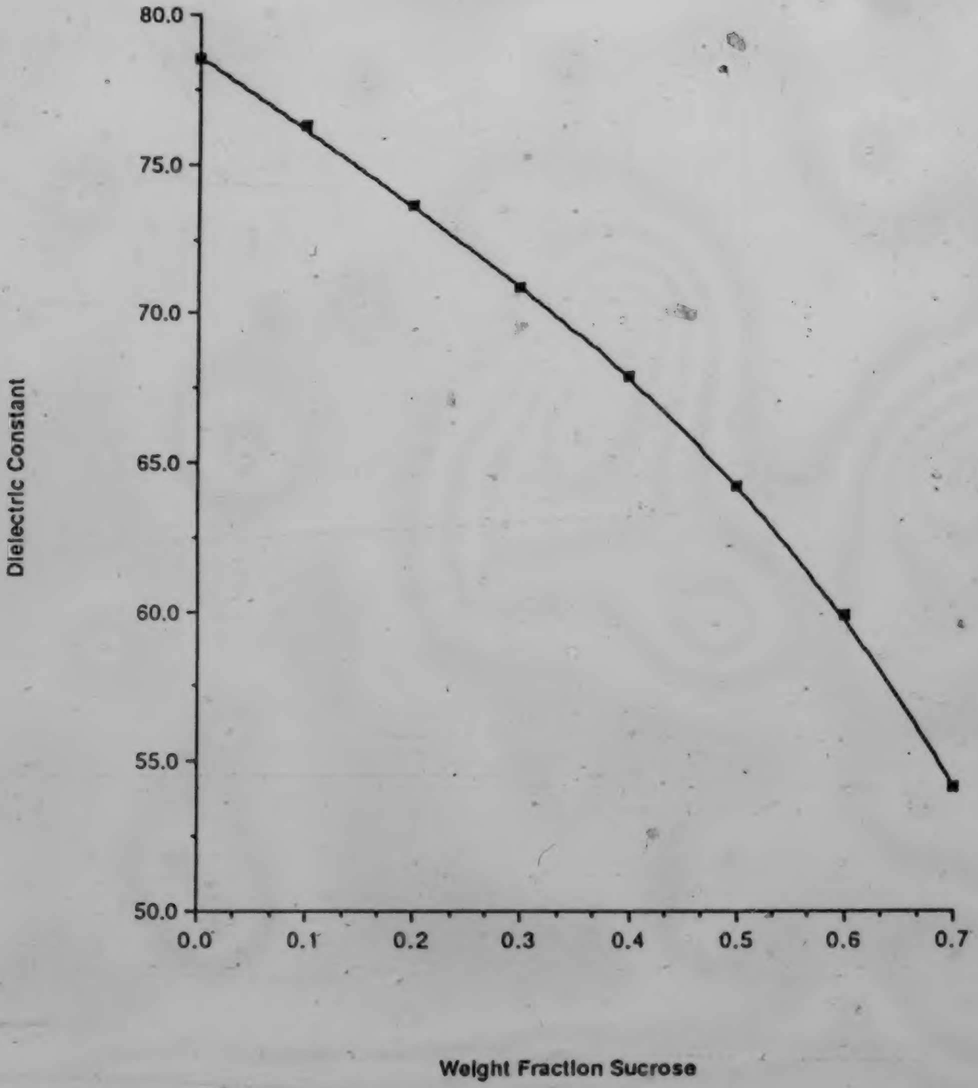

Figure 10.3 Correlation of the dielectric constant of aqueous sucrose solutions at 25° C. Experimental data from Harned and Owen (1958).

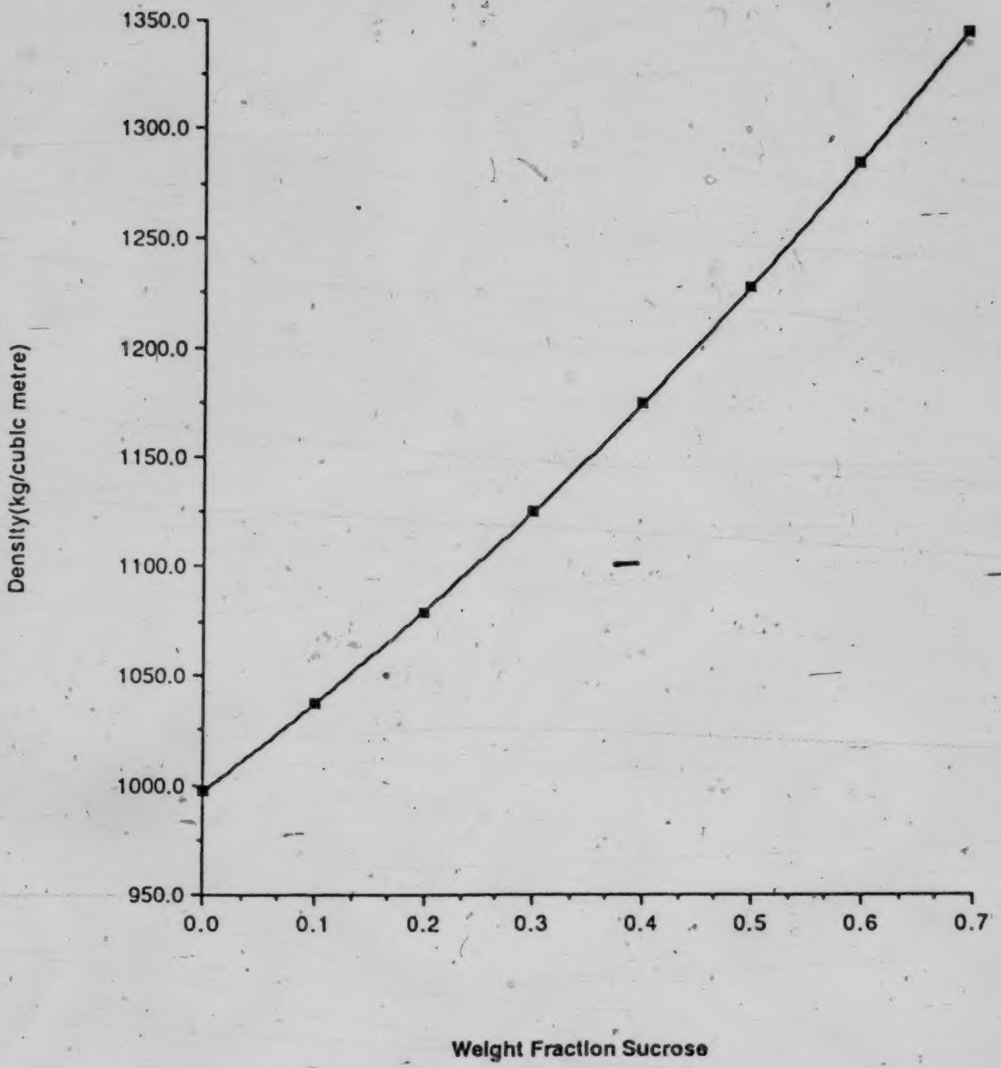

Figure 10.4 Correlation of the density of aqueous sucrose solutions at 25° C. Experimental data from Weast (1979), and Honig (1953).

11. APPENDIX 4 : Correlation of Experimental Data for Parameter Estimation

The use of numerical techniques for the optimization of the model parameters is greatly aided by the smoothing of experimental data to a fitted numerical function. To facilitate the use of these techniques, the experimental data were fitted empirically as polynomial expressions.

11.1 Aqueous Sucrose Solutions

The osmotic coefficients (ϕ) of aqueous sucrose solutions at 0, 30 and 55.7°C were estimated from osmotic pressure measurements reported by Honig (1953), using the method reported by Lewis and Randall, (1961). In binary aqueous solutions, the following relationship exists:

$$\phi = \frac{\pi \bar{v}_w \, 1000}{RT \, M_w \, m_{suc}} \qquad [11.1.1]$$

Where π is the osmotic pressure, $\bar{v}_w$ the partial molar volume of the solvent and ϕ, the osmotic coefficient. For the partial molar volume of the solvent, molar volumes of the pure solvent may be used (Lewis and Randall, 1961). These were obtained from Weast (1979). The calculated osmotic coefficients were fitted as polynomials in the sucrose molality using a BMDP multiple regression procedure. The intercept was fixed at unity to comply with the limiting behavior of the osmotic coefficient (Lewis and Randall, 1961). The linear equations were found to be most significant at all three temperatures. Table 11.1 shows the coefficients of the polynomials, the standard regression coefficient, standard error of the estimates and the concentration range over which the polynomial was fitted at the three temperatures.

Expressions for the osmotic coefficient and sucrose activity coefficient in aqueous sucrose solutions at 25°C are reported by Robinson and Stokes (1961). The expressions apply over the entire concentration range. These data are reported elsewhere also by Robinson and Stokes (1959). The two sets of values reported however, are not consistent. A BMDP step-wise regression procedure was used to fit a polynomial to the experimental osmotic coefficient and both expressions were used in the optimization of the model parameters. Based on the experimental data of Robinson and Stokes (1959) the osmotic coefficient is calculated by:

$$\phi = 1.0 + 0.4426\, m_{suc} + 4.58 \times 10^{-4}\, m_{suc}^{4} \qquad [11.1.2]$$

Where ϕ is the osmotic coefficient and m_{suc} the sucrose molality. The standard regression coefficient for this expression is 0.9998 and the standard error of the estimate, 0.0052.

From the equations derived for the osmotic coefficients, the water activity may be calculated (Stokes and Robinson, 1966). Application of the Gibbs-Duhem equation to these equations yields the molality based, unsymmetric sucrose activity coefficient (Klotz, 1964). These may be converted to the mole fraction-based activity coefficients using equation 9.1.3. This procedure is outlined as follows (Lewis and Randall, 1961).

The expression for the osmotic coefficient (ϕ) may be rearranged to yield an expression for the water activity:

$$\ln a_w = - \left[\frac{\phi \, m_{suc} \, M_w}{1000} \right] \qquad [11.1.3]$$

The Gibbs-Duhem equation applied to a binary solution may be expressed as:

$$d\ln a_w = - \frac{x_{suc}}{x_w} \, d\ln a_{suc} \qquad [11.1.4]$$

expressed in terms of molality with $\frac{x_{suc}}{x_w} = \frac{m_{suc}}{(1000/M_w)}$

$$\frac{1000}{M_w} \, d \ln a_w = -m_{suc} \, d\ln a_{suc} \qquad [11.1.5]$$

$$\frac{1000}{M_w} d\ln a_w = -m_{suc} d\ln(\gamma^*_{s,m} m_{suc}) = -d(\phi m_{suc}) \qquad [11.1.6]$$

$$d\ln\gamma^*_{suc,m} + d\ln m_{suc} = \frac{1}{m_{suc}} \phi \, dm_{suc} + d\phi \qquad [11.1.7]$$

$$d\ln\gamma^*_{s,m} = d\phi + (\phi - 1) \, d \ln m_{suc} \qquad [11.1.8]$$

$$\ln\gamma^*_{suc,m} = \phi - 1 + \int_0^m (\phi - 1) \, d \ln m_{suc} \qquad [11.1.9]$$

Based on this integration, expressions for $\ln\gamma^*_{suc,m}$ have been developed at temperatures Of 0, 25, and 55.7°C. They are summarized below:

at 0°C:

$$\ln\gamma^{*}_{suc,m} = 0.21724\ m_{suc} \qquad [11.1.10]$$

at 25°C based on the data of Robinson and Stokes (1959):

$$\ln\gamma^{*}_{suc,m} = 0.1910\ m_{suc} - 0.5727\times10^{-4}\ m_{suc}^{4} \qquad [11.1.11]$$

at 55.7°C:

$$\ln\gamma^{*}_{suc,m} = 0.17324\ m_{suc} \qquad [11.1.12]$$

These correlations are valid over the same concentration range as the corresponding expression for the osmotic coefficient (see Table 11.1).

Expressions for the apparent, relative, molal enthalpy (ϕL_s) of sucrose solutions are reported by Glucker *et al.* (1939) and Stroth and Schönert (1977) at 20, 25 and 30 °C. Using the method described by Klotz (1964), expressions for the partial molar enthalpies of the ~~sucrose~~ and water were developed. The method is summerized below (Klotz, 1964):

The apparent, relative, molal enthapy (ϕL_s) is defined by the expression:

$$\phi L_s = \phi H_s - \phi H_s^{o} \qquad [11.1.13]$$

Where ϕH_s is the apparent molal enthalpy and ϕH_s^{o} the

Table 11.1 Osmotic coefficient constants in aqueous sucrose solutions

Temperature (°C)	a[a]	Standard error of estimate[b]	R^2[b]	Range molality (mol kg^{-1})
0	.10862	0.0142	.999	0-4
30	.09787	0.0648	.987	0-5
55.7	.08662	0.0834	.989	0-4.4

---

[a] based on experimental osmotic pressures from Honig (1953); osmotic coefficient calculated from: $\theta = 1 + a\ m_s$, where m_s is the sucrose molality.

[b] obtained by stepwise regression using BMDP statistical package

apparant molal enthalpy in the infinitly dilute reference state. The partial molal enthalpy of the solute ($\bar{h}_s$) is calculated from the relative apparent molal heat content (ϕL_s) using the following relationship (Klotz, 1964):

$$\bar{h}_s = \phi L_s + m_{suc} \left[\frac{\partial \phi L_s}{\partial\, m_{suc}} \right]_{n_w} \qquad [11.1.14]$$

To calculate the relative partial molal enthalpy of the solvent in aqueous solutions, the following relationship is used:

$$\bar{h}_w = \frac{m_{suc}(\phi L_s - \bar{h}_s)}{55.51} \qquad [11.1.15]$$

The expression for the reduced, partial molal enthalpies at 20, 25 and 30°C are summarized below:

at 20°C:

sucrose

$$\frac{\bar{h}_s^E}{RT} = 0.4425\ m_{suc} + 3.56\times10^{-2}\ m_{suc}^2 \qquad [11.1.16]$$

water

$$\frac{\bar{h}_w^E}{RT} = -3.986\times10^{-3}\ m_{suc}^2 + 4.24\times10^{-4}\ m_{suc}^3 \qquad [11.1.17]$$

at 25°C:

sucrose

$$\frac{\bar{h}_s^E}{RT} = 0.4544\ m_{suc} + 3.63\times10^{-2}\ m_{suc}^2 \qquad [11.1.18]$$

water

$$\frac{\bar{h}_w^E}{RT} = -4.093\times10^{-3}\ m_{suc}^2 + 4.29\times10^{-4}\ m_{suc}^3 \qquad [11.1.19]$$

at 30°C:

sucrose

$$\frac{\bar{h}^E_s}{RT} = 0.4655\times m_{suc} + 3.53\times10^{-2}\, m^2_{suc} \qquad [11.1.20]$$

water

$$\frac{\bar{h}^E_w}{RT} = -4.193\times10^{-3}\, m^2_{suc} + 4.24\times10^{-4}\, m^3_{suc} \qquad [11.1.21]$$

where $\bar{h}^E$ is the partial, molar, excess entropy. The reduced partial molar, excess entropies are calculated using the expressions above and this thermodynamic relationship (Choudhury, 1987).

water:

$$\frac{\bar{s}^E_w}{R} = \frac{\bar{h}^E_w}{RT} - \frac{\bar{g}^E_w}{RT} \qquad [11.1.22]$$

sucrose:

$$\frac{\bar{s}^E_s}{R} = \frac{\bar{h}^E_s}{RT} - \frac{\bar{g}^E_s}{RT} \qquad [11.1.23]$$

11.2 Ethanol-Sodium Chloride-Water-Systems

Smirnov and his colleagues (1980,1981) report values of the logarithm of the unsymmetric, practical, mean, activity coefficient ($\ln\gamma^*_{\pm,m}$) of sodium chloride in aqueous solutions of 0, 10, 30, 50 and 70 mol % ethanol (salt-free) at 25°C. These data, reported in graphical form, were digitized using a Calcomp digitizer and fitted as polynomials in the root of the salt molalities using the IMSL subroutine "RLFOR". The fitted polynomials were forced through the origin to reflect the boundary conditions of the unsymmetric activity coefficient. The polynomials selected were determined by statistical analysis of the explained and unexplained variation. The standard regression coefficient of each polynomial is close to unity. The polynomial coefficients are reported in Table 11.2. In all cases the % Root Mean Square of the experimental and predicted $\ln\gamma^*_{\pm,m}$ is less than 1 percent. Mole fraction-based activity coefficients are calculated from these polynomials using equation 9.2.4.

Solvent activity coefficients were estimated from experimental equilibrium vapour-phase compositions of aqueous ethanol solutions, saturated with sodium chloride under atmospheric pressure. These data are reported by Furter (1958) and Mondez-Gonzalez (1973). The method given by Van Den Berg and Bruin (1981) is used. If ideality in the gas phase is assumed, the solvent fugacity is equal to the partial pressure (P_i), and the standard state fugacity is equal to the pure component vapour pressure at the system temperature (P_i^o):

$$a_{solvent} = \frac{P_i}{P_i^o} \qquad [11.2.1]$$

Where $a_{solvent}$ is the solvent activity. To calculate the pure component vapour pressures, the Antoine constants reported by Gmehling *et al.* (1977) are used. The solvent activity coefficient ($\gamma_{solvent}$) is calculated from the solvent activity by:

Table 11.2 Coefficients for calculation of the practical mean activity coefficient of sodium chloride in aqueous ethanol solutions at 25°C

Ethanol Conc. mol % (salt-free)	A	B	C	D	E	Range molality (mol kg^{-1})
10	-2.258	3.177	-2.003	0.461	0.0	[0-4]
30	-4.423	12.822	-21.428	17.128	-5.089	[0-1.1]
50	-4.607	12.580	28.234	36.726	-18.764	[0-0.75]

Coefficients estimated using IMSL subroutine "RLFOR" based on data from Smirnov and Ovchinnikova (1981) and Smirnov *et al.* (1980).

$$\ln \gamma_{\pm,m} = Am_s^{.5} + Bm_s + Cm_s^{1.5} + Dm_s^{2} + Em_s^{2.5}$$

where m_s is the salt molality on a solvent basis.

$$\frac{a_{solvent}}{x_{solvent}} = \gamma_{solvent} \qquad [11.2.2]$$

Solvent activity coefficients, calculated from experimental data and predicted using the UNIQUAC equation are presented in Table 11.3.

11.3 Sodium Chloride-Sucrose-Water System

Expressions for the molality based solute activity coefficient at 25°C in this system are given by Robinson *et al.* (1970). It should be noted that there is a typographical error in the expression given by Robinson *et al.* (1970) for the calculation of the practical, mean, activity coefficient of sodium chloride in aqueous solution. The correct expression is as follows:

$$\begin{aligned}\log_{10}\gamma_c^o &= -.5115(m_c/m^\theta)^{1/2}/[1+1.316(m_c/m^\theta)^{1/2}] \\ &+ 0.04513(m_c/m^\theta) - 0.01113(m_c/m^\theta)^2 \\ &+ 0.00561(m_c/m^\theta)^3 - 0.000954(m_c/m^\theta)^4 \\ &+ 0.0000574(m_c/m^\theta)^5 \qquad [11.3.1]\end{aligned}$$

Where γ_c^o is the mean, practical, unsymmetric activity coefficient of sodium chloride in a binary solution of salt molality m_c, and m^θ is a standard value of molality, taken as 1 mol kg^{-1} (Robinson *et al.*, 1970).

Both these components are normalized under the unsymmetric convention. In multicomponent solvents the

Table 11.3 Vapour-liquid equilibria and solvent activity coefficients in aqueous ethanol saturated with salt

Temperature (K)	x_{water}	x_{EtOH}	y_{EtOH}	$\ln\gamma_{EtOH}$	$\ln\gamma_{water}$
360.95	.804	.041	.468	2.071	0.038
355.52	.788	.071	.553	1.908	0.096
354.05	.746	.130	.564	1.368	0.188
353.75	.725	.162	.629	1.258	0.165
353.35	.665	.250	.614	0.823	0.209
353.05	.580	.354	.633	0.574	0.307
352.35	.437	.528	.685	0.224	0.465
352.25	.387	.588	.689	0.126	0.581
350.55	.129	.865	.882	-0.016	0.782
from Mondeja-Gonzalez (1973)					
374.95	.804	.009	.001	2.07	-.080
361.55	.801	.021	.209	2.66	-.034
359.05	.791	.035	.498	2.37	-.044
355.55	.779	.068	.550	1.96	-.047
354.05	.741	.127	.615	1.42	.020
353.45	.688	.204	.628	1.02	.066
353.25	.610	.314	.650	.628	.159
352.65	.497	.458	.662	.329	.309
351.95	.359	.621	.688	.139	.504
351.45	.234	.756	.734	.049	.668
350.45	.130	.864	.800	.035	.875
351.55	.083	.913	.869	.007	.824
350.45	.055	.943	.917	.033	.903
351.05	.027	.971	.943	-.009	.921
from Furter (1958)					

system pressure 760±5 mm Hg

infinite dilution state is not straightforward (O'Connell, 1977). Infinite dilution may be defined with respect to the individual component, the solute activity coefficient approaching unity as the solute concentration approaches zero.

Sucrose:

$$\ln\gamma^{*,x,\infty}_{sucrose} \rightarrow 0 \text{ as } x_{sucrose} \rightarrow 0$$

Salt:

$$\ln\gamma^{*,x,\infty}_{\pm} \rightarrow 0 \text{ as } \Sigma x_i \rightarrow 0$$

If this convention is followed, the standard state is a function of the solution composition and temperature, The solution includes all components except the component at infinite dilution. Smirnov *et al.* (1980,1981) express their results based on this definition of the infinite dilution state. The infinite dilution state may also be defined as the pure aqueous solution. The solute activity coefficients approaching unity only when the solution concentration approaches pure water:

For all solutes:

$$\ln\gamma^{*,x,0}_{solute} \rightarrow 0 \text{ as } \Sigma x_w \rightarrow 1$$

This infinite dilution state is a function only of the system temperature. The expressions presented by Robinson *et al.* (1970) are based on this infinite dilution state. Activity coefficients normalized under these two conventions are related as follows:

$$\ln\gamma^{*,x,\infty}_i = \ln\gamma^{*,x,0}_i - \ln\gamma^{*,\infty,0}_i \qquad [11.3.2]$$

Where the second superscript refers to the solution concentration and the third, to the infinite dilution state upon which the standard state is based. ∞ denotes the solution at infinite dilution with respect to the individual solute while 0 denotes the pure aqueous solution, infinite dilution state.

The infinite dilution state with respect to the individual component was selected for this study. Infinite dilution activity coefficients are not predicted well using the UNIQUAC equation (Alessi *et al.*, 1982) and the use of this infinite dilution state to define the standard state removes the requirement that the infinite dilution activity coefficients be predicted well with the model. For this system, the molality-based activity coefficients are calculated using the expressions presented by Robinson *et al.* (1970), normalized to the selected standard state with equation 11.1.26, and transformed to the mole fraction-based activity coefficients using equation 9.1.5

11.4 Ethanol-Sucrose-Water System

The solubility of sucrose in aqueous ethanol at 14 and 20°C are reported in the International Critical Tables and by Honig (1953). To estimate the sucrose activity coefficients of the saturated solutions, an iso-activity relationship as presented by Hougen *et al.* (1954) is used.

When equilibrium is achieved between the solid and the liquid states in a solution, the fugacity of the precipitated solute is equal in both phases. If the solid phase does not change, its fugacity in the liquid phase is constant at a given temperature regardless of the solution composition (Gmehling *et al.*, 1978). This property also applys to the activity if the standard state does not change.

The aqueous sucrose phase diagram has been reported by Young and Jones (1949) and Chandrasekaran and King (1971). They report that above 5°C, anhydrous sucrose is the stable species precipitated. In solutions of aqueous ethanol saturated with sucrose, it is assumed that the pure sucrose is also precipitated. Based on this, the sucrose activity in the liquid phase is constant at a given temperature, and equal to the saturation activity of sucrose in the binary aqueous solution at the same temperature.

The activity of sucrose is expressed on a rational basis which cannot be estimated from the solid standard state for reasons previously given (Appendix 2). It may however, be calculated from experimental data using the following relationship:

$$a^*_{sat} = \gamma^*_{sat} x_{sat} \qquad [11.4.1]$$

where a^*_{sat} is the rational, saturation activity, γ^*_{sat} the rational, unsymmetric activity coefficient of sucrose at saturation and x_{sat} the mole fraction of sucrose in the saturated solution. Robinson and Stokes (1959) report a saturation mole fraction of 0.1008 at 25°C. Under these conditions, the reported sucrose activity coefficient is 1.1013 (Robinson and Stokes, 1959). Based on these values, the solubility of sucrose at this temperature in solutions of varying composition may be estimated.

The variation of the rational solute activity (a_s^*) with temperature under constant pressure is given by the relationship (Hougen *et al.*, 1954):

$$\left.\frac{\partial \ln a_s^*}{\partial T}\right]_P = \frac{(H_{s,l}^o - H_{s,s}^o)}{RT} \qquad [11.4.2]$$

Where $H_{s,l}^o$ is the partial molal enthalpy of the solute at infinite dilution at the temperature and pressure of the system and $H_{s,s}^o$ is the molal enthalpy of the solid in the solid state at the temperature and pressure of the system. The quantity ($\bar{H}_{s,l}^o - H_{s,s}^o$) is the differential heat of solution at infinite dilution.

This relationship is used to estimate the saturated sucrose unsymmetric activity at 20 and 14°C. Equation 11.27 is then applied with experimental measurements of the saturation mole fraction of sucrose in aqueous ethanol solutions to yield estimates of the sucrose unsymmetric activity coefficients. For the infinite heat of dilution, a value of 5.52 (kJ mol^{-1}) has been reported at 23°C (Lange, 1985). This value is assumed to be constant over the temperature range of interest and used in this calculation.

Sucrose activity coefficients in saturated solutions of aqueous ethanol estimated from experimental solubilities and predicted with the extended UNIQUAC equation are presented in Table 11.4. Note that the sucrose activity coefficient is normalized with respect to the pure aqueous solution.

Table 11.4 Unsymmetric saturation activity coefficients of sucrose in ethanol-water mixtures at 14 and 20°C

Temperature	x_{water}	x_{EtOH}	$x_{sucrose}$	$\ln\gamma^*_{sucrose}$
14°C[a]	.907	.000	.0937	1.38
	.858	.065	.0768	1.57
	.738	.214	.0480	2.04
	.608	.372	.0203	2.90
	.315	.684	.0012	5.44
	.098	.902	.0006	6.48
20°C[b]	.868	.041	.0906	1.36
	.836	.100	.0845	1.42
	.785	.137	.0776	1.51
	.740	.193	.0675	1.65
	.670	.273	.0566	1.83
	.610	.348	.0418	2.13
	.539	.436	.0245	2.66
	.414	.495	.0091	3.65
	.307	.691	.0015	5.42

[a] from West (1933)

[b] from Haeseler *et al.* (1968)

12. APPENDIX 5 : The Extended UNIQUAC Equation : Programme Listing

A computer programme written in Fortran 77 was developed to perform the numerical calculations in the extended UNIQUAC equation. This version of the programme is written as a subroutine for application of the equation. The subroutine is specific to the sodium chloride-sucrose-ethanol-water system. The binary and ternary sub-systems may be accessed using this subroutine, if the appropriate concentrations are set to zero. The parameter values are stored in a data block and by substituting for the appropriate parameters, this subroutine may be used to treat other systems. Further documentation is included in the programme listing.

```
******************************************************************
*
*  SUBROUTINE EXUNIQ
*
*  PURPOSE: TO CALCUATE THE NATURAL LOGARITHM OF THE ACTIVITY
*           COEFFICIENTS OF EACH COMPONENT IN QUATERNARY SOLUTIONS
*           OF WATER-ETHANOL-SUCROSE AND SODIUM CHLORIDE, USING
*           AN EXTENDED UNIQUAC EQUATION
*
*  USAGE: CALL EXUNIQ(X,T,GAMMA)
*
*  DESCRIPTION OF PARAMETERS;
*               X : A 1 X 5 MATRIX CONTAINING THE MOLE FRACTIONS OF
*                   EACH OF THE COMPONENTS IN THE SOLUTION ON A
*                   QUATERNARY BASIS (IONS AS INDIVIDUAL SPECIES).
*
*                   X(1) : WATER
*                   X(2) : ETHANOL
*                   X(3) : SUCROSE
*                   X(4) : SODIUM ION
*                   X(5) : CHLORIDE ION
*
*
*               T : TEMPERATURE OF THE SOLUTION (K).
*
*           GAMMA : A 1 X 4 MATRIX WHICH CONTAINS, UPON OUTPUT THE
*                   CALCULATED VALUE OF THE LOGARITHM OF THE
*                   ACTIVITY COEFFICIENT FOR EACH COMPONENT:WATER
*                   ETHANOL SUCROSE AND SALT IN POSITIONS: GAMMA(1),
*                   GAMMA(2), GAMMA(3),AND GAMMA(4) RESPECTIVELY.
*  REMARKS:
*          THE EXPRESSION IS ONLY VALID FOR SOLVENT COMPOSITIONS TO
*          A MAXIMUM OF 50 MOL% ETHANOL(SALT FREE BASIS) AND
*          TO 6 MOLAL SALT AND SUGAR (AQUEOUS MOLALITY).
*          THERE IS NO CHECKING OF THE SATURATION LIMIT.
*          THE PROGRAMME CHECKS ONLY THE CONSISTENCY OF THE
*          MOLE FRACTION PARAMETERS( IE SUMMATION = 1).
*          THE VALUE OF THE MEAN ACTIVITY COEFFICIENT ON A MOLE
*          FRACTION BASIS IS RETURNED FOR THE SALT IN GAMMA(4).
```

```
*
*  PROGRAMMING NOTES:
*        IN THIS SYSTEM, ALL NON-IONIC COMPONENTS ARE CONSIDERED
*        TO BE SOLVENTS (IE. WATER, ETHANOL, SUCROSE) AND THE
*        PHYSICAL PRIOPERTIES OF THE MIXED SOLVENT ARE CALCULATED
*        ON THIS BASIS.  AS NO TERNARY DATA EXIST FOR THESE
*        SYSTEMS, THE DENSITY AND DIELECTRIC CONSTANT OF THESE
*        MIXTURES ARE ESTIMATED ON THE BINARY AQUEOSU SOLUTIONS
*        AND AN APPROPRIATE MIXING RULE.  THE DEBYE-HUCKEL
*        PARAMETERS ARE CALCULATED BASED ON THE PHYSICAL
*        PROPERTIES OF THE SOLVENT MIXTURE.  FOR THE ION SIZE
*        PARAMETER,(A) A CONSTANT VALUE IS ASSUMED FOR BOTH IONS
*        IN SOLUTION (A=4.57E-8 M) (CHRISTENSEN ET AL. 1983).
*
*        THE PROGRAMME THEN CALCULATES THE CONCENTRATION OF EACH
*        COMPONENT ON THE DIFFERENT BASES REQUIRED (MOLALITY,
*        WEIGHT FRACTION, AQUEOUS MOLALITY).
*
*        THE MEAN RATIONAL ACTIVITY COEFFICIENT OF THE SALT
*        IS EXPRESSED USING THE UNSYMMETRIC CONVENTION (IE
*        NORMALIZED WITH RESPECT TO THE SALT AT INFINITE
*        DILLUTION), AND THE CONTRIBUTION DUE TO IONIC
*        INTERACTIONS IN THE INFINITELY DILUTE SOLUTION
*        IS ZERO, THEREFORE THIS TERM IS ENTIRELY
*        DETERMINED BY THE UNIQUAC CONTRIBUTATIONS AND
*        CONSEQUENTLY, THE UNSYMMENTRIC ACTIVITY COEFFICIENT
*        MAY BE CALCULATED AS THE DIFFERENCE BETWEEN
*        THE SYMMETRIC ACTIVITY COEFFICIENT
*        AND  THE UNIQUAC CONTRIBUTION CALCULATED AT
*        INFINITE DILUTION WITH RESPECT TO THE SALT.
*
*        ACTIVITY COEFFICIENTS OF IONS ARE NOT DIRECTLY
*        MEASURABLE, IN THE CASE OF THE SODIUM CHLORIDE,
*        THE RATIONAL MEAN ACTIVITY COEFFICIENT IS
*        CALCULATED AS THE GEOMETRIC MEAN OF THE INDIVIDUAL
*        ION ACTIVITY COEFFICIENTS.
*
*        SOLVENT ACTIVITY COEFFICIENTS ARE CALCULATED ON A
*        SYMMETRIC BASIS.
*
* NOTE:
*        SUCROSE ACTIVITY COEFFICIENTS ARE OFTEN EXPRESSED
*        ON AN UNSYMMETRIC BASIS. THE PROGRAMME HOWEVER,
*        DOES NOT NORMALIZE THE SUCROSE ACTIVITY COEFFICIENT.
*        THE NORMALIZATION FACTOR MAY BE CALCULATED BY
*        CALLING THE PROGRAMME AGAIN WITH THE APPROPRIATE
*        CONCENTRATIONS CORRESPONDING TO THE DESIRED INFINITE
*        DILUTION STATE.
*
*  SUBROUTINES AND FUNCTIONS REQUIRED:
*        SETTAU,SETL,UNICOM,UNIRES,DH,BG
*        THE DATA ARE STORRED IN DATA BLOCK "ION"
*
*****************************************************************
      SUBROUTINE EXUNIO(X,T,GAMMA)
        INTEGER I,K,J,N
        REAL*8 X(5),L(5),Q(5),R(5),MW(5),MOL(5),MWA(5),INDIL(5)
        REAL*8 TAU(5,5),T,GAMMA(4),BETA,A,Z(5),SUMN,U(5,5)
        REAL*8 CATU,CAT,ANU,AN,WFET,UNI,B1,BA
        REAL*8 DI,DEN,M(5),TC,QP(5),WFS(3),B2
        COMMON/ION/Q,QP,R,Z,L,MW,U
        COMMON/ION2/B1,B2

        EXTERNAL UNICOM,UNIRES,DH,BG,SETTAU


        N=5
        NSOL=3
        TC=T-273.15D0
        CALL SETTAU(N,T,U,TAU)


        SUMN=0.0D0
        SUMS=0.0D0


*CALCULATE SOLVENT WEIGHT FRACTIONS

        WSOL=0.0D0
        DO 100 I=1,NSOL
 100       WSOL=WSOL+X(I)*MW(I)

        DO 101 I=1,NSOL
 101      WFS(I)=(X(I)*MW(I))/WSOL

*CALCULATE SOLVENT BASED MOLALITIES

        DO 102 I=1,N
 102       M(I)=X(I)/WSOL

* CALCULATE AQUEOUS MOLALITIES

        DO 103 I=1,N
 103       MWA(I)=X(I)/(X(1)*MW(1))

* CALCULATE  THE INFINITE DILUTION MOLE FRACTIONS

        DO 104 I=1, NSOL
 104       INDIL(I)=X(I)/(1.0D0-(2.0D0*X(4)))


        INDIL(4)=0.0D0
        INDIL(5)=0.0D0


*     CALCULATE DIELECTRIC CONSTANT OF SOLVENT MIXTURE

         DIW=78.5400*10.0D0**(0.0580-(0.00200*TC))
         DIET=24.3000*10.0D0**(6.7600-(.27000*TC))
         DISW=DIW*WFS(1)+DIET*WFS(2)-1.052*WFS(1)*WFS(2)-
     &       16.5800*WFS(1)*(WFS(2)**2)
         DISW=DIW-10.6600*WFS(3)-41.0600*(WFS(3)**2)+
     &120.0D0*(WFS(3)**3)-183.6D0*(WFS(3)**4)+
     &74.2800*(WFS(3)**5)

        IF((WFS(2)+WFS(3)) .EQ. 0.0) THEN
           DISOL=DIW
        ELSE
        DISOL=(WFS(2)/(WFS(2)+WFS(3)))*DIEW+(WFS(3)/(WFS(2)+WFS(3)))*
     &      DISW
      ENDIF

*     CALCULATE DENSITY OF SOLVENT MIXTURE


        DENW=0.0D0
        DENW=999.83952D0+16.945176D0*TC-7.9870401D-3*TC**2
        DENW=DENW-46.170461D-6*TC**3+105.56302D-9*TC**4
        DENW=DENW-(280.54253D-12*(TC**5))
        DENW=DENW/(1.0D0+16.87985D-3*TC)

        DENSUC=DENW+380.7D0*WFS(3)+181.7D0*(WFS(3)**2)-77.15D0
*    &*(WFS(3)**3)+211.4D0*(WFS(3)**4)-135.0D0*(WFS(3)**5)
        DENET=DENW-124.2*WFS(2)-83.74D0*WFS(2)**2

      IF((WFS(2)+WFS(3)) .EQ. 0.0) THEN
          DENSOL=DENW
      ELSE IF(WFS(3) .EQ.  0.0) THEN
          DENSOL=DENET
      ELSE IF(WFS(2) .EQ.  0.0) THEN
          DENSOL=DENSUC
      ELSE
         DENSOL=1.0D0/(((1.0D0/((WFS(2)/(WFS(2)+WFS(3)))*DENET))+
     &         (1.0D0/((WFS(3)/(WFS(2)+WFS(3)))*DENSUC)))
      ENDIF


*        CALCULATE DEBYE-HUCKEL PARAMATERS

        A=1.3285760D6*(DENSOL**0.5D0)/((DISOL*T)**1.5D0)
        BA=7.2520420D0*((DENSOL/(DISOL*T))**0.5)
        BETA=50.8D0-(B1*WFS(2))-(B2*WFS(3))

*CALCULATE INDIVIDUAL ION ACTIVITIES AND UNSYMMETRIC RATIONAL MEAN
*ACTIVITY COEFFICIENT.

        CATU=UNICOM(N,4,X,Q,R,L)+UNIRES(N,4,X,QP,R,TAU)
        ANU=UNICOM(N,5,X,Q,R,L)+UNIRES(N,5,X,QP,R,TAU)
        CAT=CATU-DH(N,4,3,M,MW,Z,A,BA)+
    &BG(N,4,3,MWA,MW,T,BETA)
        AN=ANU-DH(N,5,3,M,MW,Z,A,BA)+
    &BG(N,5,3,MWA,MW,T,BETA)
*CALCULATE THE INFINITE DILUTION ACTIVITY COEFFICIENT OF THE
*INDIVIDUAL IONS

        CATIN=UNICOM(N,4,INDIL,Q,R,L)+UNIRES(N,4,INDIL,QP,R,TAU)
        ANIN=UNICOM(N,5,INDIL,Q,R,L)+UNIRES(N,5,INDIL,QP,R,TAU)

*PERFORM NORMALIZATION OF THE ION ACTIVITY COEFFICIENTS

        CAT=CAT-CATIN
        AN=AN-ANIN

        GAMMA(4)=(CAT+AN)*0.5D0


*CALCULATE SOLVENT ACTIVITY COEFFICIENTS
        DO 200 I=1,3
           UNI=UNICOM(N,I,X,Q,R,L)+UNIRES(N,I,X,QP,R,TAU)
           GAMMA(I)=UNI+DH(N,I,3,M,MW,Z,A,BA)-
    &                 BG(N,I,3,MWA,MW,T,BETA)

 200    CONTINUE
      END

*****************************************************************
*   THIS DATA BLOCK CONTAINS THE REQUIRED PARAMETERS FOR THE
*   WATER-ETHANOL-SODIUM CHLORIDE SYSTEM.
*   A BRIEF DESCRIPTION OF EACH PARAMETER WILL BE GIVEN.
*
*   DESCRIPTION OF PARAMETERS:
*
*              R : A 1 X N MATRIX CONTAINING THE VALUE OF THE
*                  UNIQUAC VOLUME PARAMETER R.
*              Q : A 1 X N MATRIX CONTAINING THE VALUE OF THE
*                  UNIQUAC AREA PARAMETER Q.
*
*              Z : A 1 X N MATRIX CONTAINING THE CHARGE VALUE OF
*                  EACH OF THE COMPONENTS IN SOLUTION.  FOR NEUTRAL
*                  SOLVENTS THIS VALUE SHOULD BE SET TO ZERO.
*
*              L : A 1 X N MATRIX  WHICH CONTAINS THE VALUES
*                  OF THE UNIQUAC L PARAMETER FOR THE COMPONENT
*                  MIXTURE.
*
*             MW : A 1 X N MATRIX CONTAINING THE VALUE OF THE
*                  MOLECULAR WEIGHT OF EACH OF THE COMPONENTS IN
*                  THE SOLUTION(KG/MOL).
*
*              U : A N X N MATRIX CONTAINING THE VALUES OF THE
*                  UNIQUAC ENERGY PARAMETERS U(I,J).
*
*          B1,B2 : BRONSTED-GUGGENHEIM SOLVENT PARAMETERS FOR
*                  AQUEOUS ETHANOL AND AQUEOUS SUCROSE RESPECTIVELY
*
*   REMARKS:THE MATRICIES HAVE BEEN INDEXED WITH THE SOLVENTS
*           TAKING THE FIRST 3 VALUES (WATER=1 ETHANOL=2 SUCROSE=3)
*           FOLLOWED BY THE CATION AND ANION AT POSITIONS 4 AND 5
*           RESPECTIVELY.
*
*
*******************************************************************
      BLOCK DATA
       REAL*8 Q(5),QP(5),R(5),Z(5),L(5),MW(5),U(5,5)
       REAL*8 B1,B2
       DATA Q/1.4D0,1.97D0,5.527D0,2.732D-1,.9917D0/
       DATA QP/1.4D0,1.97D0,5.527D0,2.732D-1,.9917D0/
       DATA R/9.2D-1,2.11D0,8.107D0,1.426D-1,0.9881D-0/
       DATA Z/0D0,0.0D0,0.0D0,1.0D0,-1.0D0/
       DATA L/-0.2320D+01,-0.4100D0,-5.2430D0,0.2044D0,-0.1410D-1/
       DATA MW/18.015D-3,46.0688D-3,342.2996D-3,22.9898D-3,35.017D-3/
       DATA U/0.0D0,-34.66D0,-55.3D0,-693.1D0,1240.1D0,
    &         280.66D0,0.0D0,124.4D0,5000.0D0,5000.0D0,
    &        -55.3D0,124.4D0,-37.4D0,2724.0D0,1130.7D0,
    &        -693.1D0,5000.0D0,2724.0D0,5.0D3,0.0D0,
    &         1240.1D0,5000.D0,1130.7D0,0.0D0,5.0D3/
       DATA B1/77.1D0/
       DATA B2/17.34D0/
      COMMON/ION/Q,QP,R,X,L,MW,U
      COMMON/ION2/B1,B2
      END
*****************************************************************
*
*    SUBROUTINE : SETL
*
*    PURPOSE : TO CALCULATE A VECTOR OF THE UNIQUAC PARAMETER L
*              USING THE FOLLOWING FORMULA:
*              L(J) = ZC/2*(R(I)-Q(I))-(R(I)-1)
*
*    USAGE : CALL SETL(N,ZC,Q,R,L)
*
*    DESCRIPTION OF PARAMETERS:
*              N : AN INTEGER VALUE CONTAINING THE NUMBER OF
*                  COMPONENTS IN THE SOLUTION.
*
*             ZC : THE VALUE OF THE LATTICE COORDINATION NUMBER
*
*              Q : A 1 X N MATRIX CONTAINING THE VALUE OF THE
*                  UNIQUAC VOLUME PARAMETER Q.
*              R : A 1 X N MATRIX CONTAINING THE VALUE OF THE
*                  UNIQUAC AREA PARAMETER R.
*
*              L : A 1 X N MATRIX  WHICH UPON OUTPUT CONTAINS
*                  THE VALUES OF L FOR THE COMPONENT MIXTURE.
*
*       NOTE:
*             THIS SUBROUTINE IS NOT USED IN SUBROUTINE EXUNIQ.
*             IT IS INCLUDED HERE FOR REFERENCE PURPOSES.
*
*****************************************************************
      SUBROUTINE SETL(N,ZC,Q,R,L)
         INTEGER N
         REAL*8 Q(N),R(N),L(N),Z
         DO 100, I=1,N
 100        L(I)=(ZC*0.5D0)*(R(I)-Q(I))-(R(I)-1.0D0)
         RETURN
         END
*****************************************************************
*
*    SUBROUTINE : SETTAU
*
*    PURPOSE : TO CALCULATE THE MATRIX OF UNIQUAC ENERGY
*              PARAMETERS (TAU(I,J) FORM A MATRIX OF INTERACTION
*              PARAMETERS(U(I,J)) USING THE FORMULA:
*                 TAU(I,J) = EXP(-(U(I,J)-U(J,J))/T)
*
*    USAGE : CALL SETTAU(N,T,U,TAU)
*
*    DESCRIPTION OF PARAMETERS:
*              N : AN INTEGER VALUE CONTAINING THE NUMBER OF
*                  COMPONENTS IN THE SOLUTION.
*
*              T : THE TEMPERATURE OF THE SOLUTION (K).
*
*              U : A N X N MATRIX CONTAINING THE VALUES OF THE
*                  UNIQUAC ENERGY PARAMETERS U(I,J) (K).
*
*            TAU : A N X N MATRIX CONTAINING UPON OUTPUT, THE
*                  UNIQUAC INTERACTION PARAMETERS TAU(I,J).
*
*****************************************************************
      SUBROUTINE SETTAU(N,T,U,TAU)
         INTEGER N,I,J
         REAL*8 T,U(N,N),TAU(N,N)

         DO 100 I=1,N
            DO 101 J=1,N
 101           TAU(I,J)=DEXP(-((U(I,J)-U(J,J))/T))
 100     CONTINUE

         RETURN
         END
*****************************************************************
*
*  FUNCTION : UNICOM
*
*  PURPOSE : THIS FUNCTION CALCULATES THE COMBINATORIAL CONTRIBUTION
*            TO THE UNIQUAC EQUATION FOR THE LOGARITHM OF THE
*            ACTIVITY COEFFICIENT  OF THE COMPONENT SPECIFIED.
*
*    USAGE : VAR = UNICOM(N,I,X,Q,R,L)
*
*    DESCRIPTION OF PARAMETERS:
*
*              N : AN INTEGER VALUE CONTAINING THE NUMBER OF
*                  COMPONENTS IN THE SOLUTION.
*
*              I : AN INTEGER VALUE CONTAINING THE INDEX OF THE
*                COMPONENT IN QUESTION.
*
*              X : A 1 X N MATRIX CONTAINING THE MOLE FRACTION OF
*                  EACH OF THE COMPONENTS IN THE SOLUTION.
*
*              R : A 1 X N MATRIX CONTAINING THE VALUE OF THE
*                  UNIQUAC VOLUME PARAMETER R.
*              Q : A 1 X N MATRIX CONTAINING THE VALUE OF THE
*                  UNIQUAC AREA PARAMETER Q.
*
*              L : A 1 X N MATRIX  WHICH CONTAINSTHE VALUES OF THE
*                  UNIQUAC L PARAMETER OF THE COMPONENT MIXTURE.
*
*****************************************************************
      FUNCTION UNICOM(N,I,X,Q,R,L)
         INTEGER N,I,J,K
         REAL*8 Q(N),R(N),L(N),X(N),SUMRX,SUMQX,SUMXL
         REAL*8 TEMP
         SUMRX=0.0
         SUMQX=0.0
         SUMXL=0.0

         DO 100 K=1,N
            SUMRX=SUMRX+R(K)*X(K)
            SUMQX=SUMQX+Q(K)*X(K)
            SUMXL=SUMXL+X(K)*L(K)
 100     CONTINUE

         UNICOM=DLOG(R(I)/SUMRX)+5.0D0*Q(I)*DLOG((Q(I)*SUMRX)/(R(I)*
    &SUMQX))+L(I)-(R(I)/SUMRX)*SUMXL
```

```
      RETURN
      END
**********************************************************************
*
*  FUNCTION : UNIRES
*
*   PURPOSE : THIS FUNCTION CALCULATES THE RESIDUAL CONTRIBUTION
*             TO THE UNIQUAC EQUATION FOR THE LOGARITHM OF THE
*             ACTIVITY COEFFICIENT  OF THE COMPONENT SPECIFIED.
*
*     USAGE : VAR = UNIRES(N,I,X,Q,R,TAU)
*
*    DESCRIPTION OF PARAMETERS:
*
*                 N : AN INTEGER VALUE CONTAINING THE NUMBER OF
*                     COMPONENTS IN THE SOLUTION.
*
*                 I : AN INTEGER VALUE CONTAINING THE INDEX OF THE
*                   COMPONENT IN QUESTION.
*
*                 X : A 1 X N MATRIX CONTAINING THE MOLE FRACTION OF
*                     EACH OF THE COMPONENTS IN THE SOLUTION.
*
*                 R : A 1 X N MATRIX CONTAINING THE VALUE OF THE
*                     UNIQUAC VOLUME PARAMETER R.
*                 Q : A 1 X N MATRIX CONTAINING THE VALUE OF THE
*                     UNIQUAC AREA PARAMETER Q.
*
*               TAU : A N X N MATRIX  WHICH CONTAINS THE VALUES OF THE
*                     UNIQUAC INTERACTION PARAMETERS (TAU(I,J)).
*
***********************************************************************
      FUNCTION UNIRES(N,I,X,Q,R,TAU)
        INTEGER N,I,J,K,L
        REAL*8 X(N),Q(N),R(N),TAU(N,N)
        REAL*8 SI(10),FE(10),SUMQX,SUMRX,SSITAU

        SUMQX=0.0D0
        SUMRX=0.0D0
        SSITAU=0.0D0

        DO 100 K=1,N
           SUMRX=SUMRX+R(K)*X(K)
           SUMQX=SUMQX+Q(K)*X(K)
 100    CONTINUE

        DO 101 K=1,N
           SI(K)=Q(K)*X(K)/SUMQX
           FE(K)=R(K)*X(K)/SUMRX
           SSITAU=SSITAU+SI(K)*TAU(K,I)
 101    CONTINUE

        T2=0.0D0
        DO 102 K=1,N
           SUM=0.0
           DO 103 L=1,N
 103          SUM=SUM+SI(L)*TAU(L,K)
           T2=T2+SI(K)*TAU(I,K)/SUM
 102    CONTINUE

        UNIRES=-Q(I)*DLOG(SSITAU)+Q(I)-Q(I)*T2
        RETURN
        END
*********************************************************************
*
*  FUNCTION : DH
*
*   PURPOSE : THIS FUNCTION CALCULATES THE DEBYE-HUCKEL CONTRIBUTION
*             TO THE EXTENDED UNIQUAC EQUATION FOR THE LOGARITHM OF
*             THE  ACTIVITY COEFFICIENT  OF THE COMPONENT SPECIFIED.
*             THE PROGRAMME CALCULATES THE CONTRIBUTION TO LN GAMMA
*             OF ONE OF THE SOLVENTS FROM THE FOLLOWING EQUATION:
*
*                   GIVEN THAT X = 1+B*(I**0.5)   I=IONIC STRENGTH
*
*             FOR A SOLVENT COMPONENT
*
*                LN GAMMA(DH) = -(MW*2A/B**3)*((X-(1/X)-2*LN(X))
*
*             FOR AN ION IN SOLUTION:
*
*                LN GAMMA(DH) = -(Z**2)*A*(I**0.5)/X
*
*     USAGE : VAR = DH(N,I,NSOL,M,MW,Z,A,B)
*
*    DESCRIPTION OF PARAMETERS:
*
*                 N : AN INTEGER VALUE CONTAINING THE NUMBER OF
*                     COMPONENTS IN THE SOLUTION.
*
*                 I : AN INTEGER VALUE CONTAINING THE INDEX OF THE
*                     COMPONENT IN QUESTION.
*
*              NSOL: AN INTEGER VALUE CONTAINING THE NUMBER OF
*                     COMPONENTS  IN THE SOLVENT.
*
*                 M : A 1 X N MATRIX CONTAINING THE MOLALITY OF EACH OF
*                     THE IONS IN THE SOLUTION.(PURE WATER BASIS)
*
*                MW : A 1 X N MATRIX CONTAINING THE VALUE OF THE
*                     MOLECULAR WEIGHT OF EACH OF THE COMPONENTS IN
*                     THE SOLUTION(KG/MOL).
*
*                 Z : A 1 X N MATRIX CONTAINING THE CHARGE VALUE OF
*                     EACH OF THE COMPONENTS IN SOLUTION.  FOR NEUTRAL
*                     SOLVENTS THIS VALUE SHOULD BE SET TO ZERO.
*
*                 A : THE DEBYE-HUCKEL PARAMETER FOR THE CONDITIONS
*                     (IE. TEMP,COMP) OF THE SOLVENT IN THE SOLUTION
*                      STUDIED.
*
*                       A IS CALCULATED USING THIS EXPRESSION:
*
*                           A=1.32057025*DEN**.5/((DI*T)**.5)
*
*                 B : THE DEBYE-HUCKEL ION SIZE PARAMETER
*                      CALCULATED USING THE FOLLOWING EXPRESSION:
*
*                        [illegible]=7.2530D0*(DEN/(DI*T)**0.5
*
***************************************************************************
      FUNCTION DH(N,I,NSOL,M,MW,Z,A,B)
        INTEGER NSOL,N,I
        REAL*8 A,DEN,DI,B,SUMI,M(N),MW(I),Z(N),BI,S

        SUMI=0.0D0

        DO 100 J=NSOL+1,N
 100       SUMI=SUMI+(M(J)*Z(J)**2)

        SUMI=ABS(SUMI)
        SUMI=(SUMI*.5D0)**0.5D0
        BI=SUMI*B
        S=1.0D0+BI
* FOR SOLVENTS
        IF(I .LE. NSOL) THEN
           DH=MW(I)*2.0D0*A/(B**3)*(S-(1.0D0/S)-2.0D0*DLOG(S))
* FOR IONS
        ELSE
           DH=(Z(I)**2)*A*SUMI/S
        ENDIF
        RETURN
        END
*************************************************************************
*
*  FUNCTION : BG
*
*   PURPOSE : THIS FUNCTION CALCULATES THE BRONSTED-GUGGENHIEM
*             CONTRIBUTION TO THE EXTENDED UNIQUAC EQUATION FOR THE
*             LOGARITHM OF THE ACTIVITY COEFFICIENT OF THE THE
*             COMPONENT SPECIFIED IN THE SOLUTION UNDER THE
*             CONDITIONS SPECIFIED.  THIS VALUE IS CALCULATED
*             ACCORDING TO THE FOLLOWING EQUATIONS:
*
*             FOR A SOLVENT COMPONENT
*
*                LN GAMMA(BG) = MW* SUM(BETA(C,A)/T)*MWAT(C)*MWAT(A)
*
*             FOR AN ION IN SOLUTION:
*
*                LN GAMMA(BG) = (BETA(C,A)/T)*MWAT(A,C))/2
*
*     USAGE : VAR = BG(N,I,NSOL,MWAT,MW,T,BETA)
*
*    DESCRIPTION OF PARAMETERS:
*
*               N : AN INTEGER VALUE CONTAINING THE NUMBER OF
*                   COMPONENTS IN THE SOLUTION.
*
*               I : AN INTEGER VALUE CONTAINING THE INDEX OF THE
*                   COMPONENT IN QUESTION.
*
*            NSOL: AN INTEGER VALUE CONTAINING THE NUMBER OF
*                   COMPONENTS  IN THE SOLVENT.
*
*            MWAT : A 1 X N MATRIX CONTAINING THE MOLALITY OF EACH OF
*                   THE IONS IN THE SOLUTION.(PURE WATER BASIS)
*
*              MW : A 1 X N MATRIX CONTAINING THE VALUE OF THE
*                   MOLECULAR WEIGHT OF EACH OF THE COMPONENTS IN
*                   THE SOLUTION(KG/MOL).
*
*               T : THE TEMPERATURE OF THE SOLUTION (K).
*
*            BETA : THE BRONSTED-GUGGENHIEM PARAMETER FOR THE
*                   CONDITIONS OF THE SOLVENT (IE. TEMP,COMP) IN THE
*                   SOLUTION STUDIED.
*
***************************************************************************
      FUNCTION BG(N,I,NSOL,MWAT,MW,T,BETA)
        INTEGER N,I,NSOL
        REAL*8 MWAT(N),T,BETA,MW(N)

        BG=0.0D0

        IF (I .LE. NSOL) THEN

           BG=MW(I)*BETA*MWAT(N)*MWAT(N-1)/T

        ELSE IF(I .EQ. N)THEN
* FOR A CATION
           BG=BETA*MWAT(N-1)/T
        ELSE
* FOR AN ANION
           BG=BETA*MWAT(N)/T
        ENDIF
        RETURN
        END
```

13. APPENDIX 6 : Physical Property Estimation Using the Extended UNIQUAC equation : Programme Listings

The following group of subroutines were developed for the application of the extended UNIQUAC equation to the estimation of some physical properties in the model food system. They are designed for use in conjunction with the subroutine "EXUNIQ" (see Appendix 5).

Subroutine "FPBP" calculates the boiling point elevation or freezing point depression in aqueous solutions using the expressions presented in sections 5.1.2 and 5.1.3. Subroutines "SUGSOL" and "SELSOL" calculate the solubilities of sucrose and sodium chloride using the iso-activity and temperature relationships developed in sections 5.1.4 and 11.1.4. The vapour-liquid equilibrium relationships developed in section 5.1.4 are used in the subroutine "VLE" for the calculation of equilibrium vapour-phase compositions. Each of these subroutines requires the solution of a non-linear equation. Subroutine "RTBI" uses the bisection method (Gerald and Wheatley, 1978) to find the roots of a non-linear equation. A listing of this subroutine is also included. This subroutine may be replaced by any standard root finding scheme with only slight adjustments to the subroutines required. Detailed documentation of each of the routines is included in the programme listings.

13.1 SUBROUTINE : FPBP

```
**************************************************************
*
*  SUBROUTINE:FPBP
*
*  PURPOSE : CALCULATION OF FREEZING POINT DEPRESSION IN SOLUTIONS
*            OF WATER,ETHANOL,SODIUM CHLORIDE AND SUCROSE OR
*            BOILING POINT ELEVATIONS IN SOLUTIONS OF WATER,
*            SUCROSE AND SODIUM CHLORIDE.
*
*   USEAGE : CALL FPBP(XE,IND,DT)
*
*   DESCRIPTION OF PARAMETERS
*       XE : A 1 X 5 MATRIX CONTAINING THE MOLE FRACTION OF EACH
*            COMPONENT IN THE SOLUTION. IONS ARE TREATED AS
*            INDIVIDUAL SPECIES.  IF BOILING POINT ELEVATIONS
*            ARE DESIRED XE(2) SHOULD BE ZERO.
*
*      IND : A PARAMETER (INTEGER) INDICATING WHETHER CALCULATION OF
*            SOLUTION FREEZING POINT DEPRESSION OR BOILING POINT
*            ELEVATION IS DESIRED.  THIS PARAMETER IS GIVEN THE
*            VALUE 1 IF THE FREEZING POINT DEPRESSION IS DESIRED.
*
*       DT : UPON OUTPUT THIS PARAMETER CONTAINS THE VALUE OF THE
*            PREDICTED  FREEZING POINT DEPRESSION OR BOILING
*            ELEVATION (POSITIVE VALUE).
*            THIS PARAMETER IS ALSO USED AS AN INDICATOR OF
*            ERRORS IN THE INPUT DATA.  IF THERE IS AN ERROR
*            IN THE VALUE OF THE MOLE FRACTIONS THE SUBROUTINE
*            WITH THIS PARAMETER EQUAL TO -10.  IF THE MOLE FRACTION
*            OF ETHANOL IN THE SOLUTION IS NOT ZERO AND A BOILING
*            POINT ELEVATION CALCULATION IS DESIRED, THIS PARAMETER
*            IS RETURNED WITH THE VALUE -3.
*
*  REMARKS : THE PROGRAMME USES A ROOT FINDING ROUTINE TO
*            DETERMINE THE TEMPERATURE AT WHICH WATER IN THE
*            LIQUID PHASE AND IN A SECOND PHASE, THE SOLID
*            IN THE DETERMINATION OF THE FREEZING POINT
*            DEPRESSION AND VAPOUR IN THE CASE OF BOILING
*            POINT ELEVATION, ARE IN EQUILIBRIUM.  THE
*            THERMODYNAMIC RELATIONSHIPS USED ARE GIVEN BY WALL
*            (1956).
*
*  SUBROUTINES AND FUNCTIONS REQUIRED
*
*            RTBI,FBDT
*
******************************************************************
      SUBROUTINE FPBP(XE,IND,DT)
        INTEGER IND,FND,NIT
        REAL*8 X(5),XE(5),DT,A,B,TREF,T1,T2,SUMX,RESX

        EXTERNAL RTBI,FBDT

        COMMON/FB/X,A,B,TREF

        DO 99,K=1,5
99        X(K)=XE(K)

        SUMX=X(1)+X(2)+X(3)+X(4)+X(5)
        RESX=SUMX-1.0D0
        RESX=ABS(RESX)

*        CHECK CONSISTENCY OF DATA

        IF(RESX .GT. 1.0D-3) THEN
          DT=-10.0D0
          RETURN
        ENDIF

        IF (X(2) .NE. 0.0D0) THEN
           IF(IND .NE. 1) THEN
              DT=-3.0
              RETURN
        ENDIF

*        SET EQUATION PARAMETERS DEPENDING ON WHETHER FREEZING POINT
*        DEPRESSION OR BOILING POINT ELEVATION IS DESIRED.

        IF(IND .EQ. 1) THEN
           A=6.05D-6
           B=9.6916D-3
           TREF=273.16D0
           T2=243.16D0
        ELSE
           A=7.632011D-6
           B=3.61224D-3
           TREF=373.16D0
           T2=383.16D0
        ENDIF

        T1=TREF
        CALL RTBI(FBDT,T1,T2,1.0D-4,1.0D-3,100,.FALSE.,NIT,FND)
        DT=ABS(T1-TREF)
        RETURN
        END
******************************************************************
*   FUNCTION FBDT
*
*    USAGE : FBDT(T)=
*
*  DESCRIPTION OF PARAMETER
*
*        T : TEMPERATURE OF SYSTEM AT WHICH THE VAPOUR-LIQUID OF
*            SOLID-LIQUID EQUILIBRIA IS TO BE TESTED.
*
```

```
*  REMARKS : THE FUNCTION CALCULATES THE DIFFERENCE BETWEEN THE
*            SYSTEM TEMPERATURE ASSUMED WHEN THE COMPONENT ACTIVITY
*            COEFFICIENTS ARE CALCULATED AND THE TEMPERATURE
*            CALCULATED FOR THE SYSTEM AT THE SPECIFIED WATER
*            WATER ACTIVITY USING WALL'S (1956) EQUATIONS FOR
*            THE CALCULATION OF BOILING POINT ELEVATION / FREEZING
*            POINT DEPRESSION FROM WATER ACTIVITY.
*****************************************************************
      FUNCTION FBOT(T)
        REAL*8 X(5),T,A,B,C,GAMMA(4)
        EXTERNAL EXUNIQ
        COMMON/FB/X,A,B,TREF

        CALL EXUNIQ(X,T,GAMMA)
        C=(GAMMA(1)+LOG(X(1)))

        FBOT=((-B+(B**2-4.0D0*A*C)**0.5D0)/(2.0D0*A))-ABS(T-TREF)
        RETURN
        END
```

13.2 SUBROUTINE : SUGSOL

```
*****************************************************************
*
*  SUBROUTINE SUGSOL
*
*  PURPOSE : TO CALCULATE THE SOLUBILITY OF SUCROSE IN SOLUTIONS
*            OF WATER, ETHANOL,SUCROSE AND SODIUM CHLORIDE.
*
*   USAGE  : CALL SUGSOL(TR,XSOL,XSAT)
*
*   DESCRIPTION OF PARAMETERS:
*
*      TR : REFERENCE TEMPERATURE OF SYSTEM (K)
*
*    XSOL : A 1 X 5 MATRIX CONTAINING THE MOLE FRACTIONS OF EACH
*           COMPONENT IN THE SOLUTION EXCLUDING SUCROSE.  IONS ARE
*           TREATED AS INDIVIDUAL COMPONENTS.
*                   X(1) : WATER
*                   X(2) : ETHANOL
*                   X(3) : SUCROSE ( = 0)
*                   X(4) : SODIUM ION
*                   X(5) : CHLORIDE ION
*
*
*
*    XSAT : A 1 X 5 MATRIX WHICH UPON OUTPUT CONTAINS THE
*           COMPOSITION (MOLE FRACTION) OF THE SOLUTION AT
*           SATURATION WITH RESPECT TO SUCROSE.
*           THIS ARRAY IS ALSO USED TO  INDICATE ERRORS
*           ERRORS: A VALUE OF 0.0 GIVEN EACH ELEMENT IN THE MATRIX
*                   INDICATES AN ERROR IN THE INPUT.
*                   A VALUE OF -10.0 GIVEN TO THE THIRD ELEMENT
*                   IN THIS MATRIX INDICATES THAT THE SUBROUTINE IS
*                   UNABLE TO CALCULATE THE SATURATION LIMIT
*                   USING THE THE CHOSEN METHOD.
*
*
* REMARKS : THE INPUT MATRIX IS CHECKED FOR CONSISTENCY (SUM OF THE
*
*           MOLE FRACTIONS IS UNITY) AND FOR EQUIVALENCE IN THE ION
*           CONCENTRATIONS (SODIUM CHLORIDE BEING A SYMMETRIC
*           ELECTROLYTE)  AND RETURNS IF THERE IS AN ERROR ON THE
*           INPUT VALUES.
*           THE PROGRAMME CALCULATES THE UNSYMMETRIC ACTIVITY
*           OF SUCROSE AT SATURATION AT THE SYSTEM TEMPERATURE
*           USING THE METHOD DESCRIBED BY HOUGEN ET AL 1954.
*           THIS ACTIVITY I BASED ON THE BINARY SATURATION VALUES
*           GIVEN BY ROBINSON AND STOKES (1959).
*           THE COMPOSITION OF SUCROSE IS ADJUSTED UNTIL
*           THE SUCROSE ACTIVITY IN THE SOLUTION IS EQUAL TO
*           THE SATURATION ACTIVITY CALCULATED PREVIOUSLY
*           THE PRECIPITATION OF PURE SUCROSE IS ASSUMED.
*
*  SUBROUTINES AND FUNCTIONS REQUIRED
*
*           RTBI,FSUG,EXUNIQ.
*
*****************************************************************
      SUBROUTINE SUGSOL(TR,XSOL,XSAT)
        INTEGER NIT,FND
        REAL*8 T,X(5),XSOL(5),X1,X2,A,B,C,D,TR,XSAT(5),KSPT,KSP25
        EXTERNAL RTBI,FSUG

        COMMON/SUG/X,KSPT,T

*        INITIALIZE VARIABLES

        DO 99 J=1,5
 99        X(J)=XSOL(J)

        T=TR
*        KSP25=-1.1137D0
        KSP25=-1.0843D0
        HDIL=663.6D0
        KSPT=KSP25+(HDIL*((.3354D-2)-(1.0D0/T)))
        X1=1.0D-3
        X2=1.0D0

*        CHECK CONSISTENCY OF INPUT DATA

        SUMX=X(1)+X(2)+2*X(4)
        RES=SUMX-1.0D0
        RES=ABS(RES)

        IF(RES .GT. 1.0D-4) THEN
           XSAT(3)=-10.0D0
           RETURN
        ENDIF
```

```
*       CALL RTSI(FSUG,X1,X2,1.0D-4,1.0D-3,100,.FALSE.,NIT,FND)

*  IF SOLUTION CANNOT BE FOUND RETURN INDICATOR OTHERWISE CALCULATE
*   THE SOLUTION CONCENTRATION AT SATURATION.

        IF (FND .EQ. 4) THEN
          XSAT(3)=-1.0D0
        ELSE IF (FND .EQ. 0) THEN
          XSAT(3)=-10.0D0
        ELSE
           DO 101 I=1,5
 101           XSAT(I)=X(I)/(1.0D0+X1)
          XSAT(3)=X1/(1.0D0+X1)
        ENDIF
        RETURN
        END
******************************************************************
*  FUNCTION FSUG
*
*  USAGE VAR= FSUG(X1)
*
*  DESCRIPTION OF PARAMETER
*
*       X1 : THE CONCENTRATION OF SUCROSE WHICH WHEN ADDED
*            TO ONE MOLE OF THE SOLUTION DESCRIBED BY MATRIX X
*            WILL RESULT IN A SOLUTION SATURATED WITH SUCROSE.
*
*   REMARKS : THE FUNCTION CALCULATES THE NEW SOLUTION CONCENTRATION
*            WHEN X1 MOLES OF SUCROSE ARE ADDED THE THE ORIGINAL
*            SOLUTION.  BASED ON THIS CONCENTRATION, THE ACTIVITY
*            COEFFICIENT OF THE SUCROSE IS CALCULATED FROM THE
*            EXTENDED UNIQUAC EQUATION. THE FUNCTION RETURNS THE
*            DIFFERENCE BETWEEN THE CALCULATED SUCROSE ACTIVITY
*            AND SATURATION SUCROSE ACTIVITY
*            CALCULATED AT THE SYSTEM TEMPERATURE.  AT SATURATION,
*            THIS DIFFERENCE SHOULD BE ZERO.
*
******************************************************************
      FUNCTION FSUG(X1)
        REAL*8 GAMMA(4),X(5),KSPT,XN(5),X1,T,GINDIL(4),GSUC,XIN(5)
        EXTERNAL EXUNIQ

        COMMON/SUG/X,KSPT,T

*         CALCULATE SOLUTION CONCENTRATION

        DO 200 I=1,5
          XIN(I)=0.0D0
 200      XN(I)=X(I)/(1.0D0+X1)
        XIN(1)=1.0D0
        XN(3)=X1/(1.0D0+X1)

*         CALCULATE SUCROSE ACTIVITY COEFFICIENT

        CALL EXUNIQ(XN,T,GAMMA)
        CALL EXUNIQ(XIN,T,GINDIL)
        GSUC=GAMMA(3)-GINDIL(3)

        FSUG=KSPT-GSUC-LOG(XN(3))
        RETURN
        END
```

13.3 SUBROUTINE : SELSOL

```
******************************************************************
*
*  SUBROUTINE SELSOL
*
*  PURPOSE : TO CALCULATE THE SOLUBILITY OF SALT IN SOLUTIONS
*            OF WATER, ETHANOL,SUCROSE AND SODIUM CHLORIDE.
*
*   USAGE   : CALL SUGSOL(TE,XE,SOL)
*
*   DESCRIPTION OF PARAMETERS:
*
*       TE : REFERENCE TEMPERATURE OF SYSTEM (K)
*
*       XE : A 1 X 5 MATRIX CONTAINING THE MOLE FRACTIONS OF EACH
*            COMPONENT IN THE SOLUTION EXCLUDING SODIUM CHLORIDE.
*            IONS ARE TREATED AS INDIVIDUAL COMPONENTS.
*                   X(1) : WATER
*                   X(2) : ETHANOL
*                   X(3) : SUCROSE
*                   X(4) : SODIUM ION (=0)
*                   X(5) : CHLORIDE ION (=0)
*
*      SOL : A 1 X 5 MATRIX WHICH UPON OUTPUT CONTAINS THE
*            COMPOSITION (MOLE FRACTION) OF THE SOLUTION AT
*            SATURATION WITH RESPECT TO SODIUM CHLORIDE
*            THIS ARRAY IS ALSO USED TO  INDICATE ERRORS
*            ERRORS: A VALUE OF 0.0 GIVEN EACH ELEMENT IN THE MATRIX
*                    INDICATES AN ERROR IN THE INPUT.
*                    A VALUE OF -10.0 GIVEN TO THE FOURTH ELEMENT
*                    IN THIS MATRIX INDICATES THAT THE SUBROUTINE IS
*                    UNABLE TO CALCULATE THE SATURATION LIMIT
*                    USING THE THE CHOSEN METHOD.
*
* REMARKS : THE INPUT MATRIX IS CHECKED FOR CONSISTENCY (SUM OF THE
*          MOLE FRACTIONS IS UNITY AND RETURNS AN ERROR IF THERE
*          IS AN ERROR ON THE INPUT VALUES.
*          THE PROGRAMME CALCULATES THE UNSYMMETRIC ACTIVITY
*          OF SALT AT SATURATION AT THE SYSTEM TEMPERATURE
*          USING THE EQUATION GIVEN BY CHEN (1986).
*          THIS ACTIVITY IS BASED ON THE BINARY SATURATION VALUES.
*          THE COMPOSITION OF SALT IS ADJUSTED UNTIL
*          THE SALT ACTIVITY IN THE SOLUTION IS EQUAL TO
*          THE SATURATION ACTIVITY CALCULATED PREVIOUSLY.
*          THE PRECIPITATION OF PURE SODIUM CHLORIDE IS ASSUMED.
*
```

```
*  SUBROUTINES AND FUNCTIONS REQUIRED
*
*          RTBI,FSEL,EXUNIO.
*
******************************************************************
      SUBROUTINE SELSOL(TE,XE,SOL)
         INTEGER NIT,FND
         REAL*8 T,X(5),SOL(5),X1,X2,A,B,C,D,TE,XE(5),KSP
         EXTERNAL RTBI,FSEL

         COMMON/SOL/X,KSP,T

*         INITIALIZE VARIABLES

         DO 99 J=1,5
 99         X(J)=XE(J)

         T=TE
         A=-64.669D0
         B=355.94D0
         C=16.2296D0
         D=-4.5253D-2


         DO 100 I=1,5
 100        SOL(I)=0.0D0

*         CHECK CONSISTENCY OF INPUT DATA

         SUMX=X(1)+X(2)+X(3)
         RES=SUMX-1.0D0
         RES=ABS(RES)

         IF(RES .GT. 1.0D-4) THEN
            SOL(3)=0.0D0
            RETURN
         ENDIF

*         CALCULATE SATURATION SALT ACTIVITY AT SOLUTION TEMPERATURE

          KSP=A+(B/T)+(C*LOG(T))+(D*T)

          X1=1.0D-3
          X2=1.0D0

          CALL RTBI(FSEL,X1,X2,1.0D-4,1.0D-4,100,.FALSE.,NIT,FND)

*  IF SOLUTION CANNOT BE FOUND RETURN INDICATOR OTHERWISE CALCULATE
*   THE SOLUTION CONCENTRATION AT SATURATION.

          IF (FND .EQ. 4) THEN
             SOL(4)=-1.0D0
          ELSE IF (FND .EQ. 0) THEN
             SOL(4)=-10.0D0
          ELSE
             DO 101 I=1,5
 101            SOL(I)=X(I)/(1.0D0+2*X1)
             SOL(4)=X1/(1.0D0+2*X1)
             SOL(5)=SOL(4)
          ENDIF
          RETURN
          END
*****************************************************************
*  FUNCTION FSEL
*
*  USAGE VAR= FSEL(X1)
*
*  DESCRIPTION OF PARAMETER
*
*        X1 : THE CONCENTRATION OF SUCROSE WHICH WHEN ADDED
*             TO ONE MOLE OF THE SOLUTION DESCRIBED BY MATRIX X
*             WILL RESULT IN A SOLUTION SATURATED WITH SALT.
*
*   REMARKS : THE FUNCTION CALCULATES THE NEW SOLUTION CONCENTRATION
*             WHEN X1 MOLES OF SALT ARE ADDED THE THE ORIGINAL
*             SOLUTION.  BASED ON THIS CONCENTRATION, THE MEAN
*             ACTIVITY COEFFICIENT OF THE SALT IS CALCULATED
*             FROM THE EXTENDED UNIQUAC EQUATION.  THE FUNCTION
*             RETURNS THE DIFFERENCE BETWEEN THE CALCULATED MEAN
*             SALT ACTIVITY AND THE SATURATION SALT ACTIVITY
*             CALCULATED AT THE SYSTEM TEMPERATURE.  AT SATURATION,
*             THIS DIFFERENCE SHOULD BE ZERO (TOLERANCE VALUE).
*
******************************************************************
      FUNCTION FSEL(X1)
         REAL*8 GAMMA(4),X(5),KSP,XN(5),X1,XIN(5),GIN(4)
         EXTERNAL EXUNIO

         COMMON/SOL/X,KSP,T

*         CALCULATE SOLUTION CONCENTRATION

         DO 200 I=1,5
            XIN(I)=0.0D0
 200        XN(I)=X(I)/(1.0D0+2*X1)

         XN(4)=X1/(1.0D0+2*X1)
         XN(5)=XN(4)
         XIN(1)=1.0D0
*         CALCULATE SALT ACTIVITY COEFFICIENT

         CALL EXUNIO(XN,T,GAMMA)
         FSEL=2.0D0*LOG(XN(4))+2.0D0*(GAMMA(4))-KSP
         RETURN
         END
```

13.4 SUBROUTINE : VLE

```
***************************************************************
*
*  SUBROUTINE:VLE
*
*  PURPOSE : CALCULATION OF VAPOUR-LIQUID EQUILIBRIA IN SOLUTIONS
*            OF WATER,ETHANOL,SODIUM CHLORIDE AND SUCROSE
*
*   USEAGE : CALL VLE(XE,PT,T,Y)
*
*   DESCRIPTION OF PARAMETERS
*
*        XE : A 1 X 5 MATRIX CONTAINING THE MOLE FRACTION OF EACH
*             COMPONENT IN THE SOLUTION. IONS ARE TREATED AS
*             INDIVIDUAL SPECIES.
*
*        PT : THE TOTAL PRESSURE OF THE SYSTEM EXPRESSED IN MM HG.
*
*         T : TEMPERATURE UPON OUTPUT THIS PARAMETER
*             CONTAINS THE TEMPERATURE OF THE SYSTEM.
*
*         Y : A 1 X 2 MATRIX WHICH UPON OUTPUT CONTAINS THE
*             EQUILIBRIUM VAPOUR COMPOSITIONS COMPONENT 1 IS WATER,
*             COMPONENT 2, ETHANOL.
*
*  REMARKS : THE PROGRAMME USES A ROOT FINDING ROUTINE TO
*            DETERMINE THE TEMPERATURE AT THE TOTAL PRESSURE
*            IS EQUIVALENT TO THE SUM OF THE COMPONENT
*            VAPOUR PRESSURES.  IDEALITY IN THE GAS PHASE
*            IS ASSUMED. THE METHOD USED IS GIVEN BY
*            VAN DEN BERG AND BRUIN (1981).
*            THE CONSISTENCY OF THE INPUT MOLE FRACTIONS
*            ARE CHECKED AND IF IN ERROR A NEGATIVE
*            VALUE IS RETURNED AS THE VAPOUR PHASE
*            COMPOSITION.
*
*  SUBROUTINES AND FUNCTIONS REQUIRED
*
*            RTBI,VPW, VPE,VL, EXUNIQ
*
********************************************************************
      SUBROUTINE VLE(XE,PT,T,Y)
         REAL*8 X(5),XE(5),Y(2),T,T1,T2,GAMMA(4),PT,PTOT
         INTEGER NIT,FND

         EXTERNAL VL,RTBI,EXUNIQ,VPE,VPW

         COMMON/VAPLIQ/X,PTOT

         PTOT=PT

         DO 99,K=1,5
99          X(K)=XE(K)

*         CHECK CONSISTENCY OF DATA

         SUMX=X(1)+X(2)+X(3)+X(4)+X(5)
         RES=SUMX-1.0D0
         RES=ABS(RES)

         IF(RES .GT. 1.0D-3) THEN
            Y(1)=-10.0D0
            Y(2)=-10.0D0
           RETURN
         ENDIF

*         FIND TEMP AT WHICH PTOTAL = SUM OF VAPOUR PRESSURE.

         T1=323.15D0
         T2=393.15D0

         CALL RTBI(VL,T1,T2,1.0D-3,1.0D-3,100,.FALSE.,NIT,FND)

*         CALCULATE EQUILIBTIUM VAPOUR PHASE COMPOSITION

         CALL EXUNIQ(X,T1,GAMMA)
              Y(1)=(EXP(GAMMA(1))*(VPW(T1))*X(1))/PTOT
              Y(2)=(EXP(GAMMA(2))*(VPE(T1))*X(2))/PTOT
              T=T1
          RETURN
          END
***************************************************************
*
*   FUNCTION VPW
*
*  PURPOSE : CALCULATION OF WATER VAPOUR PRESSURE USING
*             ANTOINE EQUATION.  ANTOINE CONSTANTS FROM
*             GMEHLING ET AL, 1977.
*
*  USAGE    : VAR = VPW(TEMP)
*
* PARAMETERS REQUIRED:
*
*     TEMP : SYSTEM TEMP (K)
*
*****************************************************************
     FUNCTION VPW(TEMP)
        REAL*8 A,B,C,TC,TEMP
              A=8.07131D0
              B=1730.63D0
              C=233.426D0
             TC=TEMP-273.15D0
             VPW=10.0D0**(A-(B/(TC+C)))
             RETURN
             END
***************************************************************
*
*   FUNCTION VPE
*
*  PURPOSE : CALCULATION OF ETHANOL VAPOUR PRESSURE USING
*             ANTOINE EQUATION.  ANTOINE CONSTANTS FROM
*             GMEHLING ET AL, 1977.
*
*  USAGE    : VAR = VPE(TEMP)
```

```
*
* PARAMETERS REQUIRED.
*
*     TEMP : SYSTEM TEMP (K)
*
******************************************************************
      FUNCTION VPE(TEMP)
         REAL*8 A,B,C,TC,TEMP
            A=8.3210900
            B=1718.1000
            C=237.5200
           TC=TEMP-273.1500
           VPE=10.0D0**(A-(B/(TC+C)))
           RETURN
           END
*****************************************************************
*
*   FUNCTION VL
*
*  PURPOSE : FUNCTION REQUIRED TO CALCULATE RESIDUAL
*            PRESSURE BETWEEN REQUIRED PRESSURE AND
*            SUM OF VAPOUR PRESSURES. REQUIRED FOR RTBI
*
*  USAGE   : VAR = VL(TEMP)
*
* PARAMETERS REQUIRED:
*
*     TEMP : SYSTEM TEMP (K)
*
******************************************************************
      FUNCTION VL(TEMP)
         REAL*8 GAM(4),X(5),TEMP,PTOT
           EXTERNAL VPW,VPE,EXUNIQ
           COMMON/VAPLIQ/X,PTOT

           CALL EXUNIQ(X,TEMP,GAM)

           VL=(EXP(GAM(1))*VPW(TEMP)*X(1)
     &+EXP(GAM(2))*VPE(TEMP)*X(2))-PTOT
           RETURN
           END
```

13.5 SUBROUTINE : RTBI

```
*******************************************************************
      SUBROUTINE RTBI(FN,X1,X2,XTOL,YTOL,NTOL,PDET,NIT,FND)
*
*      THIS SUBROUTINE SOLVES A NON-LINEAR EQUATION USING THE
*      BISECTION TECHNIQUE. (REFERENCE:GERALD AND WHEATLY P.6).
*
*      ARGUMENTS AND VARIABLES:
*
*      FN(X) : FUNCTION DEFINING EQUATION TO BE SOLVED.  MUST BE
*              A REAL FUNCTION, RETURNING THE VALUE OF THE FUNCTION
*              AT X (A REAL NUMBER).
*
*      X1     :LOWER BOUND ON RANGE IN WHICH ROOT IS TO BE FOUND
*
*      X2     :UPPER BOUND ON RANGE OF ROOT.
*             X1&X2 MUST BRACKET THE ROOT
*
*      XTOL   :TOLERANCE OR PRECISION ON THE VALUE OF THE ROOT
*
*      YTOL   :TOLERANCE ON THE VALUE OF THE FUNCTION AT THE ROOT
*               IE ABS|FN(ROOT)| < YTOL
*
*      NTOL   : MAXIMUM NUMBER OF ITERATIONS TO BE PERFORMED.
*             (INTEGER)
*
*      PDET   : PRINT DETAILS(LOGICAL) = .TRUE. FOR ITERATION
*               DETAIL PRINTING
*
*      RETURNED ARGUMENTS:
*
*      NIT    : NUMBER OF ITERATIONS PERFORMED
*      FND    : RETURN CODE:
*                 = 0      : ERROR ON INPUT VALUES
*                 = 1      : ROOT FOUND WITHIN YTOL LIMITS
*                 = 2      :ROOT FOUND; BOTH TOLERANCE CRITERIA
*                           SATISFIED
*                 = 3      : ROOT NOT FOUND TO WITHIN YTOL LIMITS
*                            BUT XTOL LIMITS EXCEEDED.
*                 = 4      : MAX NUMBER OF ITERATIONSREACHED
*                            ROOT NOT FOUND.
*      X1     : ROOT OR CLOSEST ESTIMATE OF THE ROOT IS RETURNED
*               AS X1.
*
*      OTHER VARIABLES:
*
*      FX1,FX2,FX3 : VALUE OF THE FUNCTION AT XI
*
*      X3          : NEXT GUESS OF ROOT
*
*
*******************************************************************
        REAL X1,X2,XTOL,YTOL
        REAL FX1,FX2,FX3,X3
        INTEGER NTOL,NIT,FND
        LOGICAL PDET

        FX1=FN(X1)
        FX2=FN(X2)
```

```
*        CHECK INPUT DATA AND ECHO DETAILS IF REQUIRED

         IF(ABS(FX1) .LT. YTOL ) THEN
            FND=1
            NIT=0
            RETURN
         ELSE IF(ABS(FX2) .LT. YTOL) THEN
            X1=X2
            FND=1
            NIT=0
            RETURN
         ENDIF

         YTOL=ABS(YTOL)
         XTOL=ABS(XTOL)

         IF(PDET) THEN
            WRITE(2,1000) 'X TOLERANCE= ', XTOL
            WRITE(2,1000) 'Y TOLERANCE= ', YTOL
            WRITE(2,1001) 'MAXIMUM # ITERATIONS= ',NTOL
         ENDIF

         IF((FX1*FX2).GT.0.0 )THEN
            FND=0
            NIT=0
            X1=0.0
            IF(PDET) THEN
               WRITE(2,1)
            ENDIF
            RETURN
         ENDIF
    1    FORMAT(T5,'DATA ERROR')

         IF(PDET) THEN
            WRITE(2,1002)
         ENDIF

1000     FORMAT(T5,A,E10.3)
1001     FORMAT(T5,A,I4)
1002     FORMAT(/T2,'ITERATION #',T17,'X1',T28,'X2',T43,'X3',T57,
     &'F(X1)',T70,'F(X2)',T83,'F(X3)')

         DO 100 I=1,NTOL

*            CALCULATE NEW VALUE OF X

            X3=(X1+X2)*0.5

            FX3=FN(X3)

            IF (PDET) THEN
            WRITE(2,1003)I,X1,X2,X3,FX1,FX2,FX3
            ENDIF

1003        FORMAT(T6,I2,T10,E12.6,T23,E12.6,T36,E12.6,T53,E12.6,
     &T66,,E12.6,T81,E12.6)

*            CHECK CONVERGENCE, IF NOT WITHIN TOLERANCE LIMITS
*            CALCULATE NEW GUESS

            IF(ABS(X2-X1) .GT. XTOL) THEN
               IF(ABS(FX3).GT. YTOL) THEN
                  IF((FX3*FX1) .LT. 0.0) THEN
                     X2=X3
                     FX2=FX3
                  ELSE
                     X1=X3
                     FX1=FX3
                  ENDIF

               ELSE IF(ABS(FX3) .LT. YTOL) THEN
                  FND=2
                  NIT=I
                  X1=X3
                  RETURN
               ENDIF

            ELSE IF(ABS(FX3) .LT. YTOL) THEN
               FND=2
               NIT=I
               X1=X3
               RETURN
            ELSE
               FND=3
               NIT=I
               X1=X3
               RETURN
            ENDIF
100     CONTINUE

        FND=4
        NIT=NTOL
        X1=X3
        RETURN
        END
```